# A CONDUCTOMETRIC STUDY OF THE REACTION VELOCITIES OF 2,4-DINITROCHLORO, BROMO, AND IODOBENZENE WITH PIPERIDINE IN DIMETHYLSULFOXIDE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

---

A Thesis

Presented to

The School of Graduate Studies

Drake University

---

In Partial Fulfillment

of the Requirements for the Degree

Master of Arts

---

by

Fred Moosreiner

January 1980

# A CONDUCTOMETRIC STUDY OF THE REACTION VELOCITIES OF 2,4-DINITROCHLORO, BROMO, AND IODOBENZENE WITH PIPERIDINE IN DIMETHYLSULFOXIDE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

by

Fred Moosreiner

Approved by Committee:

L. Emmett Wilcox
Chairperson

James B. Lindberg

Dean of the School of Graduate Studies

# A CONDUCTOMETRIC STUDY OF THE REACTION VELOCITIES OF 2,4-DINITROCHLORO, BROMO, AND IODOBENZENE WITH PIPERIDINE IN DIMETHYLSULFOXIDE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

An abstract of a Thesis by
Fred Moosreiner
January 1980
Drake University
Advisor: Dr. F. E. Jacob

The problem. C. O. Frank and T. R. Berkland have followed the kinetics of the reaction of 2,4-dinitrohalobenzene with piperidine in ethanol using a conductometric method. L. E. Youngberg concluded that this method permits greater precision than either the titrimetric or spectrophotometric techniques which involve quenching of reaction aliquots.

Significant reaction rate increases have been observed for certain reaction types when protic solvents are replaced with dipolar aprotic solvents, which are not readily explainable in terms of such physical properties as dielectric constant. Since data in dipolar aprotic solvents is random, the above system was studied in dimethyl sulfoxide to determine the applicability of the conductometric method, rate constants, activation energies and entropies, and halogen reactivity series.

Procedure. After checking the chloro analog in ethanol, piperidine and 2,4-dinitrochloro, bromo, and iodobenzene were reacted in dimethyl sulfoxide at three temperatures and two temperatures.

Findings. The revised average rate for the chloro analog in ethanol was 1.691 l $mol^{-1}$ $min^{-1}$ ± .094. The average rate constants for the chloro, bromo, and iodo analogs in dimethylsulfoxide at 25.0°C were 142.2 ± 11.9, 111.2 ± 8.7, and 20.04 l $mol^{-1}$ $min^{-1}$ ± 0.48, and at 35.0°C the average rate constants were 195.2 ± 20.0, 165.7 ± 19.2, and 30.62 l $mol^{-1}$ $min^{-1}$. There are no comparable data by other methods.

Conclusions. The 2,4-dinitrohalobenzene series reacts 50 to 90 times faster in dimethylsulfoxide than in ethanol. This is in agreement with the increases reported for the 4-nitrohalobenzene series. However, the iodo analog of the latter series increased 350 times. The halogen reactivity series is Cl>Br>>I and Cl>>Br>I in terms of rate constants and activation energies respectively.

Recommendations. The design of an automated system of data collection could be investigated. The application of this technique to quantitative determinations and analysis of amine mixtures also offers an area for study.

TABLE OF CONTENTS


| | PAGE |
|---|---|
| INTRODUCTION | 1 |
| LITERATURE REVIEW | 5 |
| EXPERIMENTAL DESIGN | 28 |
| CALCULATIONS | 41 |
| CONCLUSIONS AND DISCUSSION | 109 |
| LITERATURE CITED | 159 |
| APPENDIX I | 165 |
| APPENDIX II | 177 |

# LIST OF TABLES


| TABLE | | PAGE |
|---|---|---|
| I. | The specific conductances of various concentrations of potassium chloride at 25°C. | 32 |
| II. | Average conductances and conductivity ratios at given times: .00100 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in ethanol. | 53 |
| III. | Average conductances and conductivity ratios at given times: .00200 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in ethanol. | 54 |
| IV. | Average conductances and conductivity ratios at given times: .00250 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in ethanol. | 55 |
| V. | Average conductances and conductivity ratios at given times: .00100 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in ethanol. | 56 |
| VI. | Average conductances and conductivity ratios at given times: .00200 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in ethanol. | 57 |
| VII. | Average conductances and conductivity ratios at given times: .00250 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in ethanol. | 58 |
| VIII. | Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 59 |
| IX. | Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 60 |
| X. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrochlorobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 61 |

TABLE PAGE

XI. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrochlorobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 62

XII. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrochlorobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 63

XIII. Average conductances and conductivity ratios at at given times: .000070 moles of 2,4-dinitrochlorobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 64

XIV. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 65

XV. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 66

XVI. Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrochlorobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 67

XVII. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrochlorobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. 68

XVIII. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrochlorobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. 69

XIX. Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrochlorobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. 70

XX. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrobromobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. 71

TABLE PAGE

XXI. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrobromobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. 72

XXII. Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrobromobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. 73

XXIII. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrobromobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 74

XXIV. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrobromobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 75

XXV. Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrobromobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. 76

XXVI. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrobromobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 77

XXVII. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrobromobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 78

XXVIII. Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrobromobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. 79

XXIX. Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitrobromobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. 80

XXX. Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitrobromobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. 81

| TABLE | | PAGE |
|---|---|---|
| XXXI. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitrobromobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. | 82 |
| XXXII. | Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitroiodobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 83 |
| XXXIII. | Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitroiodobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 84 |
| XXXIV. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitroiodobenzene in cell 1 at 25.0°C in dimethyl sulfoxide. | 85 |
| XXXV. | Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitroiodobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. | 86 |
| XXXVI. | Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitroiodobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. | 87 |
| XXXVII. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitroiodobenzene in cell 1 at 35.0°C in dimethyl sulfoxide. | 88 |
| XXXVIII. | Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitroiodobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. | 89 |
| XXXIX. | Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitroiodobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. | 90 |
| XL. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitroiodobenzene in cell 2 at 25.0°C in dimethyl sulfoxide. | 91 |

| TABLE | | PAGE |
|---|---|---|
| XLI. | Average conductances and conductivity ratios at given times: .000025 moles of 2,4-dinitroiodobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. | 92 |
| XLII. | Average conductances and conductivity ratios at given times: .000050 moles of 2,4-dinitroiodobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. | 93 |
| XLIII. | Average conductances and conductivity ratios at given times: .000070 moles of 2,4-dinitroiodobenzene in cell 2 at 35.0°C in dimethyl sulfoxide. | 94 |
| XLIV. | Reproductivity of cell 1 and cell 2 at various concentrations of KCl at 25.0°C. | 109 |
| XLV. | Slopes, Y-intercepts, and coefficients of determination for the 2,4-dinitrochloro-benzene reaction at 25.0°C in ETOH. | 112 |
| XLVI. | Rate constant, half-life, and reaction order for the 2,4-dinitrochlorobenzene reaction at 25.0°C in ETOH. | 113 |
| XLVII. | Extrapolated and measured $C_o$ values for Frank, Berkland and this study for 2,4-dinitrochlorobenzene at 25.0°C in ETOH. | 115 |
| XLVIII. | Recalculated reaction rates for Frank, Berkland and this study for the 2,4-dinitrochlorobenzene reaction at 25.0°C in ETOH. | 117 |
| XLIX. | Ratios of the infinity conductances for various concentrations of 2,4-dinitrochlorobenzene at 25.0°C in ETOH. | 119 |
| L. | Ratios of the initial conductances for various concentrations of 2,4-dinitrochlorobenzene at 25.0°C in ETOH. | 121 |
| LI. | Analysis of variance of experimenters, concentrations, and cells for the reaction of 2,4-dinitrochlorobenzene with piperidine at 25.0°C in ETOH. | 123 |

| TABLE | | PAGE |
|---|---|---|
| LII. | Slopes, Y-intercepts, and coefficients of determination for the 2,4-dinitrochlorobenzene reaction in DMSO at various concentrations and temperatures. | 127 |
| LIII. | Rate constant, half-life, and reaction order for the 2,4-dinitrochlorobenzene reaction in DMSO at various concentrations and temperatures. | 128 |
| LIV. | Ratios of the infinity conductances for various concentrations of 2,4-dinitrochlorobenzene in DMSO. | 130 |
| LV. | Extrapolated and measured initial conductances for the 2,4-dinitrochlorobenzene reaction in DMSO. | 131 |
| LVI. | Ratios of the initial conductances for various concentrations of 2,4-dinitrochlorobenzene in DMSO. | 132 |
| LVII. | Ratios of infinity conductances at 35.0°C to 25.0°C for the 2,4-dinitrochlorobenzene reaction in DMSO. | 132 |
| LVIII. | Slopes, Y-intercepts, and coefficients of determination for the 2,4-dinitrobromobenzene reaction in DMSO at various concentrations and temperatures. | 133 |
| LIX. | Rate constant, half-life, and reaction order for the 2,4-dinitrobromobenzene reaction in DMSO at various concentrations and temperatures. | 134 |
| LX. | Ratios of the infinity conductances for various concentrations of 2,4-dinitrobromobenzene in DMSO. | 136 |
| LXI. | Extrapolated and measured initial conductances for the 2,4-dinitrobromobenzene reaction in DMSO. | 137 |
| LXII. | Ratios of the initial conductances for various concentrations of 2,4-dinitrobromobenzene in DMSO. | 137 |

| TABLE | | PAGE |
|---|---|---|
| LXIII. | Ratios of infinity conductances at 35.0°C to 25.0°C for the 2,4-dinitrobromobenzene reaction in DMSO. | 138 |
| LXIV. | Slopes, Y-intercepts, and coefficients of determination for the 2,4-dinitroiodobenzene reaction in DMSO at various concentrations and temperatures. | 139 |
| LXV. | Rate constant, half-life, and reaction order for the 2,4-dinitroiodobenzene reaction in DMSO at various concentrations and temperatures. | 140 |
| LXVI. | Ratios of the infinity conductances for various concentrations of 2,4-dinitroiodobenzene in DMSO. | 141 |
| LXVII. | Extrapolated and measured initial conductances for the 2,4-dinitroiodobenzene reaction in DMSO. | 142 |
| LXVIII. | Ratios of the initial conductances for different concentrations of 2,4-dinitroiodobenzene in DMSO. | 142 |
| LXIX. | Ratios of the infinity conductances at 35.0°C to 25.0°C for the 2,4-dinitroiodobenzene reaction in DMSO. | 14 |
| LXX. | Average rate constants, energies of activation, and entropies for the reaction of 2,4-dinitrohalobenzene with piperidine in DMSO. | 143 |
| LXXI. | Average rate constants, energies of activation, and entropies for the reaction of 2,4-dinitrohalobenzene with piperidine in ETOH. | 146 |
| LXXII. | Average rate constants, energies of activation, and entropies for the reaction of 4-nitrohalobenzene with piperidine in DMSO. | 148 |
| LXXIII. | Limiting ionic conductances of halide ions in selected protic and aprotic solvents at 25.0°C. | 149 |
| LXXIV. | Hydrogen bonding activity coefficient of the anion. | 150 |

LIST OF FIGURES


| FIGURE | | PAGE |
|---|---|---|
| 1. | The reaction of 2,4-dinitrohalobenzene with piperidine. | 2 |
| 2. | Paths of reaction of 4-nitrohalobenzene with piperidine (ref. 67). | 14 |
| 3. | Specific solvation of the 4-nitrohalophenyl piperidinium and 2,4-dinitrohalophenyl piperidinium intermediates by DMSO (ref. 61). | 17 |
| 4. | DMSO-amine and amine-amine hydrogen bonding (ref. 71). | 17 |
| 5. | The large anion-large molecule assumption: $^{o}y^{s}_{B^-} = {}^{o}y^{s}_{C}$ (ref. 8). | 23 |
| 6. | $S_NAr$ transition state with a secondary amine (ref. 8). | 23 |
| 7. | Simple acid-base scheme for $S_NAr$ reactants, transition state, and products (ref. 77, 78). | 25 |
| 8. | Paths of reaction of 2,4-dinitrohalobenzene with a primary or secondary amine (ref. 90). | 43 |
| 9. | Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with ETOH in cell 1 at 25.0°C. | 95 |
| 10. | Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with ETOH in cell 2 at 25.0°C. | 96 |
| 11. | Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 1 at 25.0°C. | 97 |
| 12. | Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 2 at 25.0°C. | 98 |
| 13. | Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 1 at 35.0°C. | 99 |

FIGURE PAGE

14. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 2 at 35.0°C. 100

15. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 1 at 25.0°C. 101

16. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 2 at 25.0°C. 102

17. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 1 at 35.0°C. 103

18. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 2 at 35.0°C. 104

19. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 1 at 25.0°C. 105

20. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 2 at 25.0°C. 106

21. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 1 at 35.0°C. 107

22. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 2 at 35.0°C. 108

23. Suggested scheme for decomposition of dimethyl sulfoxide (ref. 98). 125

24. Carbon-halogen bond length versus the hydrogen bonding activity coefficient of the halide leaving group for 2,4-dinitrohalobenzene (ref. this work). 152

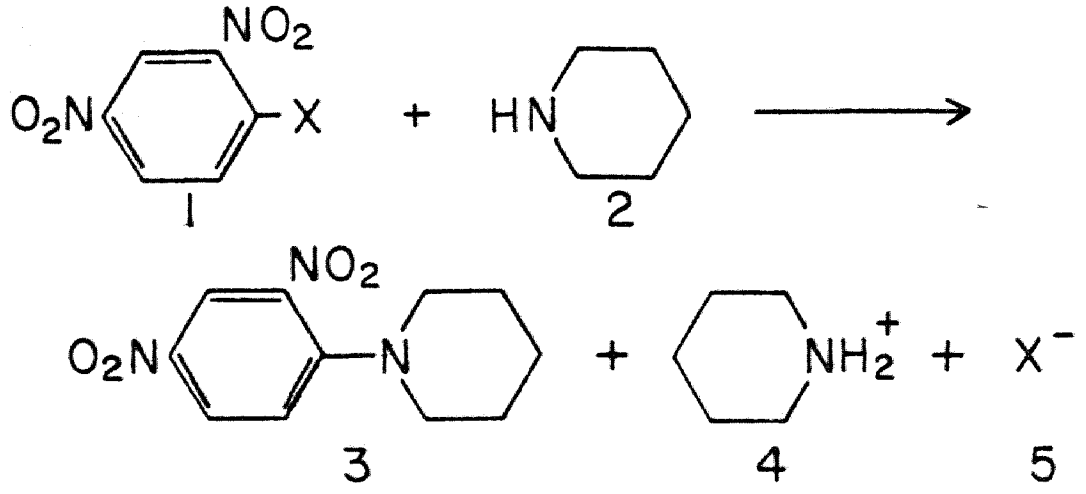
25. Carbon-halogen bond length versus the hydrogen bonding activity coefficient of the halide leaving group for 4-nitrohalobenzene (ref. 68). 153

# CHAPTER I

## INTRODUCTION

Chemical kinetics is the quantitative study of chemical reaction rates, of the velocity at which a chemical system attains equilibrium, and of the factors which influence reaction velocity, such as temperature, concentration, solvent, pressure, and catalyst. The emphasis in chemical kinetics has been the compilation of data on the rates of specific reactions with an aim toward improving technical processes, elucidation of reaction mechanisms, and studies of general principles of reactivity (1).

Charles O. Frank (2) and Terrill R. Berkland (3) have demonstrated that the reaction velocities of 2,4-dinitrohalobenzenes with piperidine in 95 percent ethanol can be followed by a conductometric method. As this reaction (Figure 1) proceeds to completion there is an increase in the concentration of piperidinium (4) and halide (5) ions which produces an increase in the conductance of the solution with time. The conductance method is applicable to reactions in which an increase or decrease in solution conductance with respect to time can be described by a linear function of concentration, from which the reaction rate constant can be calculated (4). The advantage of the conductance




X = F , Cl, Br, I .

Figure 1. The reaction of 2,4-dinitrohalobenzene with piperidine.

method over chemical methods (5) is the ability to continuously monitor the system (4).

In the conductance method the charged species should be fully ionized to provide a linear correlation between the conductance of the solution and the concentration of reactants. A good solvent for conductance studies should have a low specific conductance and should solvate charged species well, thereby limiting ion pair formation, which could result in a non-linear correlation (5,6).

Frank and Berkland in their studies used 95 percent ethanol as the reaction solvent. Ethanol solubilized both reactants and products. Ethanol (ETOH) is a protic solvent capable of contributing hydrogen to form strong hydrogen bonds.

Since 1960, interest in non-aqueous (aprotic, dipolar aprotic) solvents and the corresponding solvent effects on reaction rates has increased (7,8,9,10). Dipolar aprotic solvents are defined as solvents with a dielectric constant greater than 15, which cannot donate hydrogen atoms to form strong hydrogen bonds (10). Examples of such solvents are acetone, acetamide, benzonitrile, dimethylacetamide, dimethylformamide, dimethylsulfoxide, nitrobenzene, and nitromethane.

Differences in physical properties between dipolar aprotic solvents and the solvent replaced are not sufficient to account for the rate enhancements observed (10). For

certain reactions, rate increases of a million-fold have been observed upon changing the reaction solvent from a protic solvent such as methanol to a dipolar aprotic solvent such as dimethylsulfoxide (DMSO) or dimethylformamide (DMF) (8).

It was the purpose of this study to: 1) determine if the conductometric method of measuring reaction rate velocities used by Frank and Berkland was applicable to reactions carried out in the dipolar aprotic solvent DMSO, 2) establish a halogen reaction series for the reaction between 2,4-dinitrohalobenzene and piperidine in DMSO, 3) calculate the energy and entropy of activation for the reaction of 2,4-dinitrochloro, bromo, and iodobenzene with piperidine in DMSO, and 4) compare the results obtained by this physical method with results obtained by other methods.

# CHAPTER II

## LITERATURE REVIEW

William Nicholsen and Sir Anthony Carlise, in 1800, decomposed water with an electric current and thus was born the field of electrochemistry (11). Baron C. J. von Grotthuss, in 1805, formulated a hypothesis on the mechanism of electrolysis in which an instantaneous dissociation of molecules was caused by an electric current passing through a solution. The negative pole attracted a hydrogen atom from a water molecule. The altered water molecule would continue to the positive pole where an oxygen atom would be liberated (12).

The views held by Grotthuss met with opposition and were revised by Faraday, Hittorf, and Clausius. In 1857, Clausius modified the Grotthuss theory by denying the idea that an electric current breaks the molecules apart. He reasoned that a very large E.M.F. would be needed; but this was contrary to the experimental evidence that even a small E.M.F. would produce decomposition (13). To account for this experimental evidence, Clausius proposed that some of the electrically charged particles (ions) already existed in the solution in an uncombined state. G. Quincke and F. Kohlraush concurred with this explanation and used the

dissociation hypothesis to explain the migration of ions and conductivity (14,15). Arrhenius, using Van't Hoff's work on osmotic pressures, provided further evidence that these particles exist in an uncombined state in solution (15).

In 1876, F. Kohlrausch perfected a precise technique for measuring the conductance of a solution (16). An alternating current of low intensity, produced by an induction coil, was employed. This was coupled with a Wheatstone bridge, invented by C. Wheatstone in 1834, which was modified through the addition of a slide wire in one arm by Kirchoff (17). With this apparatus, Kohlrausch was able to accurately determine the resistance, or conductance, of an electrolyte. One arm of the bridge consisted of a cell containing the solution of unknown resistance; another arm consisted of a decade resistance box of sufficient magnitude to permit an approximate determination of the cell resistance value; and the remaining two arms of the bridge were a divided slide wire. Headphones were used to detect a null-point, which indicated the bridge was balanced. Kohlrausch found that polarization of shiny platinum electrodes was minimized by electroplating finely divided platinum upon them from a chloroplatinic acid solution (18). Jones and Bollinger (19) found that a trace of lead acetate added to the chloroplatinic acid solution, used in electroplating, increased the durability of the platinum black coating.

They also found that the lowering of cell resistance from the true value due to capacitative shunt between the parts of the cell of opposite polarity could be eliminated through proper cell design (20). Horovaka and Mendenhall (21) determined that a cathode-ray tube was as sensitive as previous null-point detectors and was better than earphones for work involving a large number of measurements.

In 1850, the first kinetic measurements were carried out by L. Wilhelmy (22). He measured the rate of inversion of sucrose and investigated the influence of concentration upon the rate of reaction. He found that the rate of reaction at any instant was proportional to the concentration of the unconverted sucrose. In 1860, Berthelot and St. Gilles performed rate studies on the hydrolysis of esters, reaching conclusions in agreement with Wilhelmy that reaction rate is proportional to the concentration of unreacted material. They found the rate of combination for an acid and an alcohol was proportional to the product of the two concentrations (22). In 1867, Harcourt and Esson investigated the reaction of potassium permanganate with oxalic acid and calculated the second order rate constant by a method similar to currently used techniques (22).

From 1888 to 1966 there have been several investigations of reaction rate by measuring the resistance of a solution. The most notable among these are: 1) reaction between ethanol and acetic acid (23), 2) reaction between

ethanol and hydrochloric acid (24), 3) hydrolysis of organic acids (25,26), and 4) reactions in benzene between silver melissilate, lead stearate, copper oleate, and others, with hydrochloric acid (27). These represented the first conductometric studies with an organic solvent. Others include: 5) nitroethane with water and deuterium oxide (28), 6) saponification of esters (29), 7) reaction of 2,4-dinitrochlorobenzene with piperidine in ethanol (2), 8) solvolysis of tertiary-butyl chloride (30), 9) alkyl halides with potassium iodide in acetone (31), 10) diphenyl chloromethane and ethanol (32), and 11) 2,4-dinitrobromo and iodobenzene with piperidine in ethanol (3). Reaction 11) was followed by monitoring the change in conductance with respect to time. From this the reaction rate was determined.

Opstall, in 1933, investigated the reaction rate between 2,4-dinitrochlorobenzene and piperidine by titration of the chloride produced with silver nitrate and found the reaction to be second order (33). During the 1950's this reaction was intensively investigated in the study of $S_NAr$ mechanism of substitution. Some examples of the types of reactions studied toward this end are: 2,4-dinitrohalobenzenes--with 1) N-methyl aniline in ethanol and in nitrobenzene (34), 2) aromatic primary amines (35), 3) benzoate (36), 4) piperidine in dioxane, methanol, and ethanol (37,33), 5) piperidine and no solvent (39), and 6) sulfite in aqueous ethanol (40); nitrohalobenzenes with 7) piperidine

in benzene (41,42), 8) piperidine in dioxane, ethanol, and methanol (43), 9) piperidine in xylene (44), 10) sodium methoxide in ethanol (45); the halonapthalenes and nitro-halonapthalenes with 11) piperidine in ethanol (46), and 12) piperidine and no solvent (47,48). These reactions have been studied in protic solvents or aprotic solvents of low dielectric constant with the exception of the reaction in nitrobenzene.

The kinetics for these reactions with piperidine have been determined by volumetric and/or spectrophotometric methods, but with the exception of the studies by Frank and by Berkland they have not been examined using a conducto-metric method. Youngberg (49) has compared the volumetric, spectrophotometric, and conductometric techniques for following the reaction of 2,4-dinitrochlorobenzene with piperidine (Figure 1) concluding the conductometric measure-ments have greater precision.

There are several reviews (50,51,52,53) which examine the versatility of DMSO as a reaction solvent and its general solvent properties. DMSO is included in Brønsted's fourth class of solvents (54). Dipolar aprotic solvents are not completely lacking in acid base properties, even though they lack the ability to form strong hydrogen bonds (54). DMSO may form dimers as well as weak 1:1 complexes due to anti-parallel, electrostatic multipolar interactions involv-ing localized polar groups rather than entire molecules (55).

DMSO is a powerful Lewis base. The negative center in DMSO is on a less hindered oxygen and interacts more strongly with a positive center than does the negative oxygen of ethanol or methanol. DMSO is a stronger base than these two protic solvents and is probably a stronger H-bond acceptor according to Parker (8).

DMSO has a high Trouton constant, but it is not thought to have a structure as highly organized as that of water. The high Trouton constant suggests strong dipole-dipole interactions between individual molecules, but less structural orientation than found in protic solvents; thus solvent reorganization seems probable (8).

In DMSO effective ionic radii are unaffected by temperature from 25°C to 55°C. Transport of ions in DMSO is limited mainly by viscous drag. The chloride, bromide, and iodide ions are only slightly solvated at 25°C, while $Li^+$, $Na^+$, and $K^+$ are solvated by 4.8, 2.8, and 2.8 DMSO molecules respectively (56).

It is widely reported (57) that DMSO solvates large ions well. That is, iodide ions should be solvated better than chloride or fluoride ions for example. This can be interpreted as steric resistance to the solvation of small ions, considered to be less significant for large ions, by bulky dipoles with the charge centered on C, S, N, or O atoms.

As a solvent DMSO dissolves most aromatic and

unsaturated hydrocarbons, organic nitrogen compounds, organosulfur compounds and many inorganic salts. It is miscible with most common organic solvents such as alcohols, ketones, lower weight esters, chlorinated solvents and aromatics. DMSO is also hygroscopic, but saturated hydrocarbons are virtually insoluble in DMSO. In viewing DMSO as a reaction solvent (58) the physical properties of interest are:

1) high polarity--the dipole moment of the sulfur-oxygen bond is 4.3 Debye units, and the molecule has a dielectric constant of 48.9 at 20.0°C,
2) aprotic nature--does not donate hydrogen for hydrogen bond formation, but solvates anions by dipolar association,
3) DMSO oxygen--slightly basic making it a good hydrogen bond donator,
4) methyl group hydrogens--replaceable only under severe conditions, when bulk $pK_a$ = 31.3,
5) specific conductance--3 x $10^{-8}$($ohm^{-1}cm^{-2}$) at 25.0°C.

DMSO has been used to facilitate the displacement of amines from heterocyclic or activated aromatic rings (59,60,61,62, 63,64,65). Part of the reason for the observed reaction rate increases with DMSO may be because it is a poor proton donor, but more probably is due to its high polarity and effect on the transition state (63,65).

Suhr (66,67,68) has extensively investigated the

$S_NAr$ reaction of neutral molecules in the solvents dimethylsulfoxide and dimethylformamide. The principle system studied was the reaction of 4-nitrohalobenzene (NXB) with piperidine (68) with emphasis placed on the reaction of the fluoro analog. Reaction kinetics were followed with a DK2A spectrophotometer. Runs were made with excess piperidine so that pseudo first order kinetics were measured.

The reaction in ethanol was only weakly dependent on solvent polarity and was much slower than in aprotic solvents of the same dielectric constant. Dependence of the rate constant on the dielectric constant of the medium (cf. equation 1) was demonstrated for the NFB reaction with piperidine at 50°C.

$$\log k = \text{const} \frac{\varepsilon - 1}{2\varepsilon + 1} \qquad (1)$$

The rate in alcohol fell below the straight line obtained by plotting the log of the rate against the dielectric constant of the solvent, while the rates in DMSO, DMF, and DMAC were above the curve.

In the case of aprotic solvents an approximate three fold increase in the rate of reaction and an activation energy of 8 kcal/mol were observed when the temperature was changed from 25°C to 50°C. The same temperature increase for the reaction in alcohol produced a five fold increase in the rate with an activation energy of 10 to 14 kcal/mol.

The slow reaction rate in ethanol is attributed to hydrogen bonding between the alcohol and the piperidine, which would lower the reactivity of the piperidine. When the nucleophile was nitroparaffin a significant rate decrease occurred because the nitroparaffin is partially in acid form and hydrogen bonding with the solvent would lower the rate. The low polarity and concentration of piperidine was considered insufficient to drastically alter the solvation of the transition state.

Piperidine participates in the decomposition of the intermediate complex I (Figure 2). Normally the substitution of chloro, bromo, or iodo compounds proceeds so slowly that it is impossible to make any clear statement about the subsequent steps in the mechanism. The rate constant k" (equation 2) was shown to include the base catalyzed decomposition of the intermediate I, because when pyridine,

$$d(II)/dt = k'(ArX)(B) + k''(ArX)(B)^2 \qquad (2)$$

unreactive with 4-nitrofluorobenzene under the experimental conditions, was added the rate of reaction increased in proportion to the pyridine concentration introduced. A similar mechanism is proposed by Brady and Cropper (69) to explain the catalysis of 2,4-nitrochlorobenzene with aliphatic amines. The second path (Figure 2) favors the transfer of a proton from a weak base to a strong base. At this point intermediate I is uncharged and decomposes into end products. For

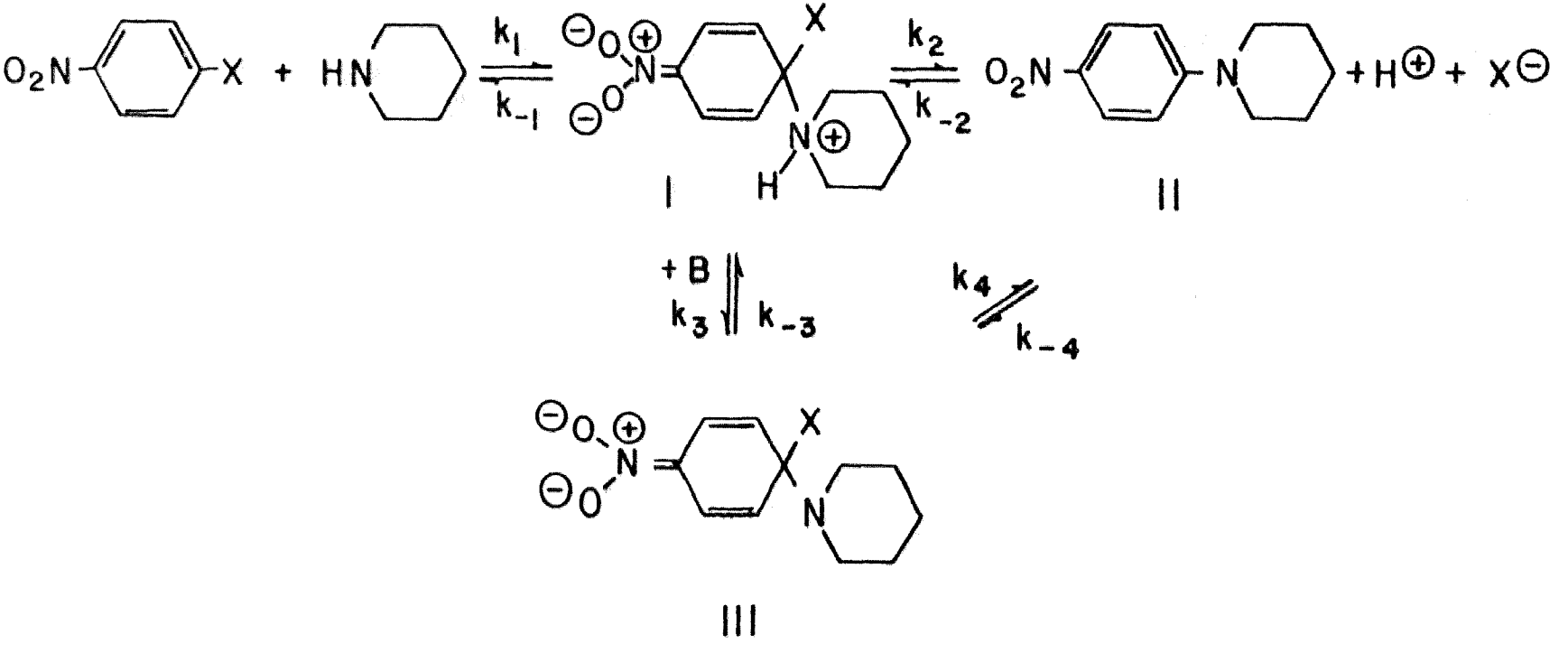



Figure 2. Paths of reaction of 4-nitrohalobenzene with piperidine (ref. 8).

fast reactions this base dependency would lie within the range of measurement error.

A minute addition of DMSO to the NFB reaction run in benzene produced a significant rate increase. Since the dielectric constant of the pure solvent was almost the same as the benzene-DMSO mixture, Suhr concluded that the high rate in DMSO cannot be attributed solely to high solvent polarity, but some other factors must also be operating. For reactions of uncharged compounds, charge separation occurs in the transition state. Non-polar solvents such as benzene do not strongly participate to any extent in transition state solvation (68).

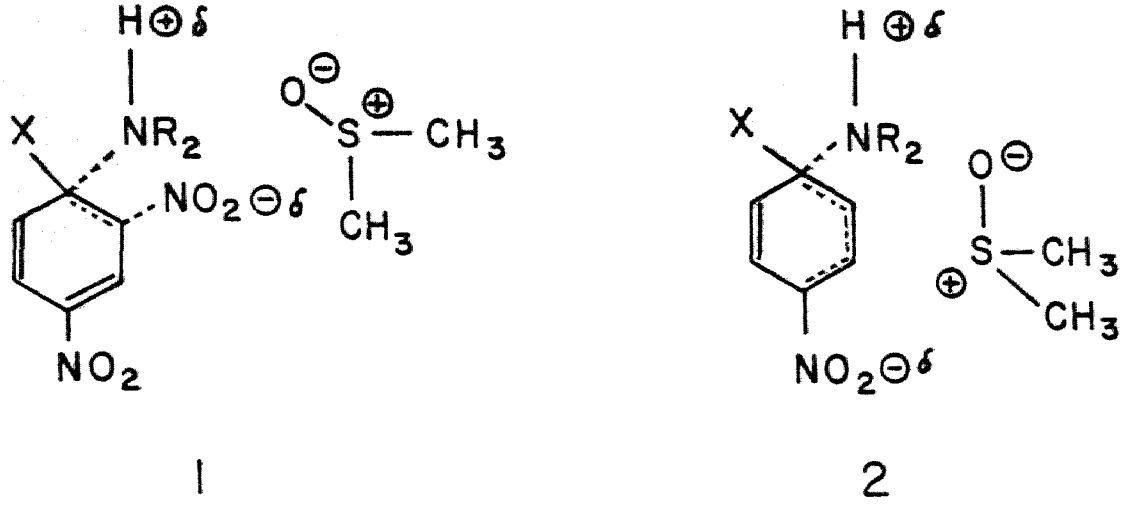
Suhr concludes that susceptibility to base catalysis can be related to high reaction rates in DMSO, DMF, and DMAC since these solvents are basic enough to remove a proton from the intermediate. The high rate of reactivity in these solvents cannot be explained by polarity. Finally, in moderately polar solvents, where k'>>k", the rate will be determined by the base catalyzed decomposition of the intermediate. In strongly polar solvents the formation of the intermediate should be the rate determining step.

Bernasconi et al. (61) measured the rates of reaction for 2,4-dinitrofluorobenzene and 2,4-dinitrochlorobenzene with piperidine as influenced by the addition of dimethylsulfoxide and p-dioxane. The reaction was catalyzed much more strongly by DMSO than pyridine, but about the same

amount as by 1,4-diaza-(2,2,2)-bycyclooctane. DMSO was shown to be much less basic than pyridine in benzene. There was a change in the dependence on piperidine concentration with the addition of DMSO, which indicates a medium effect is operating. The reaction of 2,4-dinitrochlorobenzene with piperidine is known to be insensitive to base catalysis. It is nevertheless accelerated by DMSO indicating once again that the operation of a medium effect is the primary factor in the rate acceleration and not simply base catalysis. It was only possible to measure gross medium effects through the half reaction rate constant $k_1$.

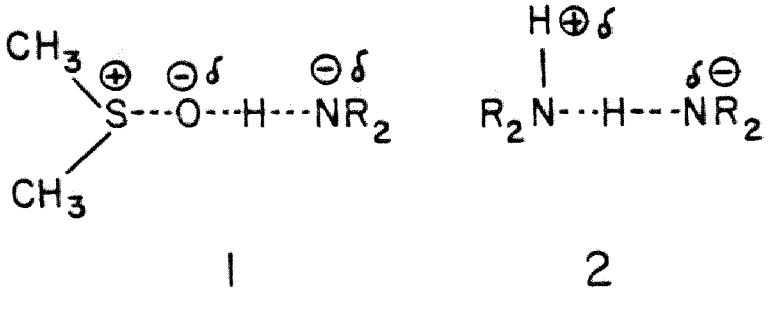
The authors indicated that it is difficult to interpret the action of DMSO. As is well known, DMSO is a rather poor solvent for small anions, but a relatively good one for large anions and dipolar structures with the negative charge delocalized as in the transition state. They concluded that a specific solvation of the transition state, as indicated in (1) of Figure 3, is the most probable form of such solvation. For the investigation of 4-nitrofluorobenzene by Suhr (68) a similar type of structure is assumed to be operating, as represented in (2); assuming that in this case two or more molecules of DMSO can lie between the positive and negative centers of the transition state.

The small increase in the rate of reaction for 2,4-dinitrochlorobenzene in chloroform and in 2-phenylethanol through nitro group binding may resemble a specific solvation



1 2

Figure 3. Specific solvation of the 4-nitrohalophenyl piperidinium and 2,4-dinitrohalophenyl piperidinium intermediates by DMSO (ref. 61).



1 2

Figure 4. DMSO-amine and amine-amine hydrogen bonding (ref. 71).

caused by the nitro group oxygen as reported by Bunnett and Garst (70) and not be dependent on base catalysis. In particular, the basicity of the nitro group is still approximately a factor of 10 less than that of DMSO.

Another interpretation (71), in which DMSO forms a hydrogen bonc complex with the amine (1) of Figure 4 and thereby the reactivity of the nucleophile is increased, would indeed satisfy the known experimental fact that both 4-nitrofluorobenzene and 2,4-dinitrochlorobenzene are catalyzed by DMSO. Then one would expect that piperidine as the stronger base would correspond to a better hydrogen bond acceptor, and from this a still stronger nucleophilic agent (2) would result. According to this, piperidine should catalyze considerably not only the reaction of 4-nitrofluro-benzene but also that of 2,4-dinitrochlorobenzene. This is not the case, so that such an interpretation cannot be envisioned. For this type of reaction Kingsbury (63) has proposed a DMSO catalysis involving polarization of the substrate by a random DMSO molecule followed by rapid nucleophilic attack on the activated species to explain the rate increase in this system.

The increase in the reaction rate when the solvent is changed from ethanol to DMSO can be viewed as a decrease in the free energy difference between the reactants and the transition state, where

$$\Delta G^{+} = \Delta H^{+} - T\Delta S^{+} \qquad (3)$$

Or in simpler terms, this rate increase is attributed to a stabilization of the transition state.

There is a general tendency for $\Delta H^{\dagger}$ and $T\Delta S^{\dagger}$ to compensate each other (72). When this occurs the observed change in $\Delta G^{\dagger}$ is not as large as that of the enthalpy or entropy. Kinetics alone cannot be used to describe this compensation effect. The actual explanation must be found in a description of solvent-solute interactions. Thus any effect which produces strong binding between a solute molecule and solvent molecules will lower the enthalpy. At the same time, this will restrict the vibrational and rotational degrees of freedom of the solvent molecules and lower the entropy. Since the transition state can occur at any point along the reaction coordinate (i.e., resemble reactants or products) and its formation and decomposition is influenced by the nature of the entering and leaving group as well as steric effects and solvent-solute interaction including electrostatic (ion-dipole, dipole-dipole), hydrogen bonding, dispersion forces and structure making and breaking, isolation of any particular factor and labeling as an effect becomes extremely difficult.

The rates of a reaction in two different solvents can be formulated in terms of absolute reaction rate theory and solvent activity coefficients of the species involved (73).

For the reaction:

$$A + B \rightarrow [X^{\dagger}] \rightarrow P \tag{4}$$

$$\bar{u}_i^s = \bar{u}_i^o + RT\ln {}^{o}\gamma^{s}_{i} \tag{5}$$

$$[X^{\dagger}] = K^{\dagger}[A][B]\ \frac{{}^{o}\gamma^{s}_{A}\ {}^{o}\gamma^{s}_{B}}{{}^{o}\gamma^{s}_{X^{\dagger}}} \tag{6}$$

$$\text{rate} = [A][B]\ \frac{KT}{h}\ k^{\dagger}\ \frac{{}^{o}\gamma^{s}_{A}\ {}^{o}\gamma^{s}_{B}}{{}^{o}\gamma^{s}_{X^{\dagger}}} \tag{7}$$

$$K_s = \frac{KT}{h}\ k^{\dagger}\ \frac{{}^{o}\gamma^{s}_{A}\ {}^{o}\gamma^{s}_{B}}{{}^{o}\gamma^{s}_{X^{\dagger}}} \tag{8}$$

${}^{o}\gamma^{s}_{i}$ of the standard solvent is unity by definition,

$$K^{o} = \frac{KT}{h}\ k^{\dagger} \tag{9}$$

$$K^{s} = K^{o}\ \frac{{}^{o}\gamma^{s}_{A}\ {}^{o}\gamma^{s}_{B}}{{}^{o}\gamma^{s}_{X^{\dagger}}} \tag{10}$$

$$\log K_s/k_o = \log {}^{o}\gamma^{s}_{Y} + \log {}^{o}\gamma^{s}_{RX} - \log {}^{o}\gamma^{s}_{YRX^{\dagger}} \tag{11}$$

The changes in solvation that occur upon transfer from ethanol to DMSO are changes in chemical potential. Even though the solvation energies of anions are approximately one order of magnitude greater than for polar molecules, the solvation energy difference of a solute (i) in two solvents may be greater for a polar molecule than for an ion. A polar solute would be expected to be more soluble

in DMSO than ethanol. This is indeed the case for dinitrohalobenzenes which are more soluble in DMSO. When a dipolar aprotic solvent like DMSO accommodates a polar solute into its solvent structure, the chemical potential would be lowered i.e., solubility increased, charge dispersal increased.

If the log ${}^{o}\gamma^{s}_{RX}$ term of equation (12) is negative this indicates that RX is more strongly solvated by DMSO than by ethanol (8). While, according to Parker (8), this can serve as indicator of relative solvation for a given substrate, determination of individual activity coefficients is nearly impossible. To simplify the problem Parker (8) and others (74) have introduced a number of extrathermodynamic assumptions.

One such assumption is termed the large anion-large molecule assumption (8) and $B^-$ and C are selected so that interactions within a given solvent, other than electrostatic,

$$ {}^{o}\gamma^{s}_{B^-} = {}^{o}\gamma^{s}_{C} \qquad (12) $$

are approximately the same. Preferably $B^-$ is very large with the negative center buried beneath ligands or non-localized. In this case, for transfer to a solvent of the same dielectric constant electrostatic interactions will remain relatively constant.

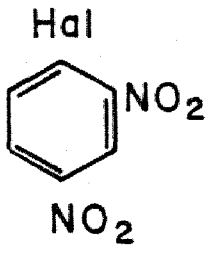
Several systems have been used as models to

represent this assumption, including the mono- and dinitrohalobenzenes as shown below in Figure 5. In this model the halide ion is a strong hydrogen bond acceptor and the transition states (2) and (4) are weak hydrogen bond acceptors. Changes in log ${}^{o}\gamma^{s}RX^{\dagger}$ would be due to entering and leaving groups and steric effects.

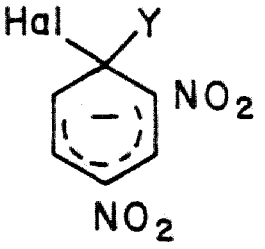
For reactions of the type represented in Figure 1, if the transition states (2) are not hydrogen bond donors, the rates of reaction for polar molecules will not be greatly enhanced when changing from a protic to dipolar aprotic solvent of similar dielectric constant but different polarity (73). Hence transition states like those in Figure 5 may complicate the reaction because of acid-base equilibria and the fact that the transition state is now a good hydrogen bond donor (73).

Parker indicates in an extensive review (8) of the effects of protic-dipolar aprotic solvents on the rates of molecular reactions that for $S_NAr$ reactions, transition states with secondary amines (Figure 6), as distinct from those for reactions of tertiary amines and dialkyl sulfides, are stronger hydrogen bond donors due to the hydrogen attached to the positive nitrogen, and as such are more strongly solvated by basic solvents like DMSO and DMF than by methanol or ethanol.

If bond breaking were significant for $S_NAr$ reactions, there would be a localization of negative charge on the

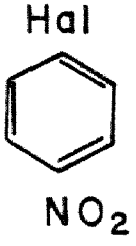



1

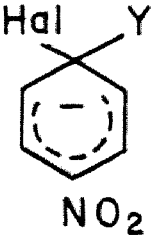



2

$$\frac{{}^{o}\gamma^{s}_{ArX}}{{}^{o}\gamma^{s}_{ArYX^{\dagger}}} = 1$$




3




4

$$\frac{{}^{o}\gamma^{s}_{ArX}}{{}^{o}\gamma^{s}_{ArYX^{\dagger}}} = 1$$

Figure 5. The large anion-large molecule assumption: ${}^{o}_{y}s_{B^-} = {}^{o}_{y}s_{C}$ (ref. 8).

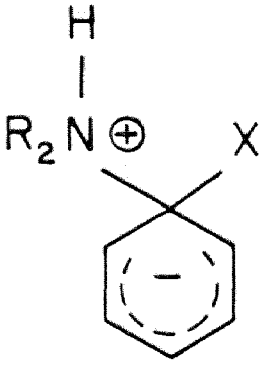



Figure 6. $S_NAr$ transition state with a secondary amine (ref. 8).

leaving halogen in the transition state. This would make fluoride a much better hydrogen bond acceptor transition state anion than iodide bearing an equivalent charge. Hence the $\delta_{hal}(\log {}^{o}\gamma^{s}\dagger)$, when s is a dipolar aprotic solvent and o is a protic solvent, should be more positive when the halogen is fluorine as compared to iodine. The polarizabilities also enhance this expected trend (8). But in fact the $\delta_{hal}$ effect is the opposite, with iodide being less negative than fluoride for the transition states compared (8). Parker concludes from this that a tight $S_NAr$ transition state anion, in which the leaving group carries very little negative charge and bond breaking has made very little progress, is consistent with the experimental evidence. In this case, bond forming with the incoming nucleophile is the rate determining step.

A view of acid and base interactions was developed in the 1960's by Pearson (75) in which an acid is defined as: a unit in which at least one atom has a vacant orbital in which a pair of electrons can be accommodated; and a base as: a unit which has at least one pair of electrons which are not already being shared in a covalent bond. The principal of hard and soft acids and bases is founded on emperical observation. In this system bases are classified as hard, soft, or borderline depending on whether they prefer to bind with the hard acid $H^+$, the soft acid $CH_3Hg^+$ or exhibit intermediate behavior. While in like fashion,

acids are classified as hard, soft or borderline depending on whether they act like the hard acid $H^+$ or the soft acid $CH_3Hg^+$. The terminology of hard and soft acids and bases (HSAB) reflecting the broader concept involved is more general than Lewis acid base theory. Through this approach hard and soft acids and bases can be viewed in terms of polarizability, size, electronegativity or other properties which permit qualitative and semi-quantitative comparison (76). Thus the principle of HSAB has utility in discussing reaction rates and offers some predictive ability with regard to reaction rates (76).

In the following scheme (Figure 7) the general acid base interactions for the kinetic reaction type of interest are described.

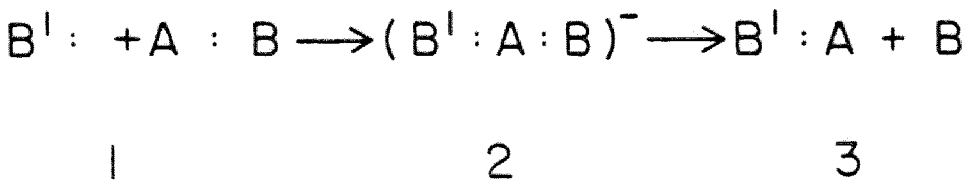



Figure 7. Simple acid-base scheme for $S_NAr$ reactants, transition state, and products (ref. 77, 78).

The transition state B':A:B can be considered an acid-base complex: A is an electrophile; B and B' are nucleophiles. Applying the terminology of HSAB "hard electrophilic centers (acids) react with hard nucleophilic centers (bases) and soft electrophilic centers react rapidly with soft nucleophiles (76,77,78). The acid-base complex (Figure 7) has an

increased coordination number and slightly longer bonds than the reactant A:B. The same considerations that predict the stability of acid:base complexes in general should also predict relative reaction rates, that is, an increased coordination number places an increased negative charge on A and makes it softer. As a corollary it can be stated that softness is more important in rate than equilibria phenomena.

For the reactions in this study, polarizability is probably the most important factor affecting reaction rate (79). From the preceding discussion, for the reaction between piperidine and 2,4-dinitroiodobenzene piperidine can be considered a borderline nucleophile; the 2,4-dinitrophenyl cation can be considered a soft electrophile; the piperidinium ion, a hydrogen bond donor, can be considered a hard acid; and the leaving halides are: chloride hard, bromide borderline, and iodide soft.

Hard acids coordinate best to the lightest atom in a family. This means the piperidinium ion would form increasingly stable complexes with the halogens in the following order $Cl \geq Br >> I$. On the other hand soft acids coordinate best to one of the heavier atoms in the same family. In other words, the 2,4-dinitrophenyl cation coordinates best with the iodide ion as evidenced by its slow rate of replacement (3). Work by Parker (8) indicates the reaction order of neutral reagents with 2,4-dinitrohalobenzene

remains unchanged, Cl$\geq$Br>>I, when going from protic to DPA solvents.

G. M. Bennett (80) synthesized 2,4-dinitroiodobenzene in 1939. Sodium iodide and 2,4-dinitrochlorobenzene in ethylene glycol were heated for 30 minutes resulting in a 30 percent yield. Bunnett and Conner (81) improved Bennett's procedure by using N,N-dimethylformamide, instead of ethylene glycol, as the reaction solvent, which resulted in a 70 percent yield of 2,4-dinitroiodobenzene (DNIB). They also found that increased refluxing time resulted in a decreased yield. It is interesting to note that an increased yield was obtained by changing the reaction solvent from a protic solvent to a dipolar aprotic solvent, dimethylformamide.

# CHAPTER III

## EXPERIMENTAL DESIGN AND CALCULATIONS

### I. Experimental Design

The problem was to determine the rate of reaction by measuring the change in conductivity of the reaction system after known times had elapsed from zero time. To determine the Arrhenius parameters the concentrations were varied over a range of $8.33 \times 10^{-4}$ to $7.0 \times 10^{-3}$ mol/ℓ and the temperature was varied over a range of 10°C.

Apparatus and preliminary work. In this study, a Model RC-18 Conductivity Bridge from Industrial Instruments, Incorporated was employed. The instrument consists of a Wheatstone bridge circuit incorporating an oscilloscope detector, A.C. circuitry for 1000 or 3000 Hz, decade dials permitting a maximum cell resistance of 111,111.1 ohms or 11,111.11 micromhos conductance, a resistance or conductance mode switch selector, a sensitivity regulator, Wagner ground, coarse and fine variable capacitors to balance cell capacitance and thereby make possible more accurate readings at higher sensitivities and an instrument ground to eliminate stray fields which would otherwise cause disturbances on the oscilloscope and contribute to a loss of sensitivity in measuring the null point. This instrument has a maximum

precision of 0.1% (82).

A double throw switch was connected between the instrument and the cells permitting readings to be taken from either of the two cells without removing the leads from the cells. All connections were made as short and kept as far apart as possible. Woven copper shielding was used to shield all connections and grounded to a water pipe (3).

Kohlrausch type cells were used. Cell 1 was constructed with the electrodes small, circular and far apart for measuring solutions of medium conductance. Cell 2 was constructed with electrodes large, concave rectangular, and close together for measuring solutions of low conductance. Cells similar to those used in this study are listed in the Fischer Catalogue (83). The cell constant of cell 1 (catalogue no. 9-366) had an approximate value of 1.3 reciprocal ohm-centimeters while the cell constant of cell 2 (catalogue no. 9-367) had an approximate value of .17 reciprocal ohm-centimers. Both cells incorporated mercury filled side arms to provide a connection between the electrodes and the external leads.

A Sargent Constant Temperature Bath (catalogue no. S-84805) was used in this study for all measurements at 25.0°C and 35.0°C. This system is equipped with a Mercurial Thermoregulator (catalogue no. S-81840 and a Thermocontroller (catalogue no. S-81995) with heating coils of 400 watts, 300 watts and 250 watts for precise control of the

temperature. The heating coils were balanced by a cooling coil which was connected to the tap water. A needle valve was used to regulate the tap water flow rate. When the temperature of the tap water exceeded 25.0°C, it was cooled in an ice bath before entering the cooling coil.

The mercury arms were cleaned periodically to prevent high resistance in this connection that would cause erroneous readings. The cleaning procedure consisted of discarding the mercury in the arms, filling the arms with dilute nitric acid, which was allowed to react until the solution stopped effervescing. Next the arms were rinsed with distilled water followed by acetone. Final drying of the arms was done by placing a small hypodermic needle connected to a vacuum into each arm for at least five minutes. The arms were then filled with fresh mercury.

The platinum electrodes were platinized to eliminate the polarization effects associated with an ac field. The cells were filled with a solution of aqua regia and the electrodes were allowed to react until they appeared to be clean (i.e. until the previous platinum black was removed and the surface appeared shiny). The cells were rinsed thoroughly with distilled water and then filled with chloroplatinic acid solution (3.0%) which contained a trace of lead acetate (0.02%) (19). Two 1.5 v cry cells were connected in series with a rheostat and an ammeter to regulate the plating current to a few tenths of an ampere. The

electrodes were evenly plated by reversing the current every thirty seconds. After plating, the cells were rinsed seven times with sulfuric acid (6N). On the seventh filling with acid, the cells were connected to the dc circuit used for the plating and the current increased until a steady gas evolution was observed at the electrodes. The current was reversed every minute for thirty minutes to remove any chlorine gas which might have been present from the preceding procedure. The cells were finally rinsed a minimum of four times with distilled water, filled with distilled water and left at room temperature for at least four hours (2,3).

Determination of cell constants. The cell constant is a function of the area of the electrodes and the distance between them. The reproducibility of the measuring system was determined by calculating the cell constant both before and after the rate studies.

Conductivity water was prepared as follows: distilled water containing a few crystals of potassium permanganate to oxidize any organic matter present was redistilled and collected warm in a polyethylene bottle. A stock solution of 0.1000 M potassium chloride was prepared using the conductivity water. In turn, solutions of 0.0100, 0.0050 and 0.0010 M potassium chloride were prepared by dilution of the stock solution.

The cell constant K (equation 13) is dependent on L, the specific conductance of the particular ions present and

R, the resistance of the solution.

$$K = L \times R \tag{13}$$

The specific conductance is the conductance of the material between parallel plates one square centimeter in area and one centimeter apart (84). Table I lists the specific conductances for standard potassium chloride solutions at 25.0°C (85).

TABLE I

THE SPECIFIC CONDUCTANCES OF VARIOUS CONCENTRATIONS OF POTASSIUM CHLORIDE AT 25°C

| KCl,M | Specific Conductance in mho/cm |
|---|---|
| 0.00100 | 0.0001469 |
| 0.00500 | 0.0007175 |
| 0.01000 | 0.001413 |

The cells were stored filled with the conductivity water both before and after using the aqueous salt solutions and were rinsed three times with each concentration before measurements were made on each concentration. The cells were filled with potassium chloride solutions and thermostated at 25.0°C. After temperature equilibrium was established, as evidenced by the nearly constant readings, 10 readings were taken on four aliquots of each

concentration. The average resistances were used to calculate the cell constant for each cell.

The volume of each cell was determined so that solutions of the desired reactant concentrations for each cell could be prepared. The volume for cell 1 was 40.0 ml and for cell 2 the volume was 20.0 ml.

The 2,4-dinitrochlorobenzene reaction in ethanol (ETOH). In order to become familiar with the measuring system and also check the reproducibility of the work of both Frank and Berkland, their 2,4-dinitrochlorobenzene (DNCB) solutions were prepared and reacted with piperidine in ethanol.

Following the procedure developed by Frank and Berkland, the 2,4-dinitrochlorobenzene solutions were prepared in order that 30.0 ml in cell 1 and 10.0 ml in cell 2 contained the required number of moles. The number of moles used in both cells was 0.0010 mol, 0.0020 mol and 0.0025 mol which corresponded to 0.0333, 0.0667 and 0.0833 mol/ℓ in cell 1 and 0.1000, 0.2000 and 0.2500 mol/ℓ in cell 2. The piperidine was prepared so that twice the number of moles of 2,4-dinitrohalobenzene would be present in the cell to react with the substrate in a second order reaction. Eastman reagent grade 2,4-dinitrochlorobenzene, recrystallized from ethanol (mp. 51-52°C), was placed in a 250 ml volumetric flask for cell 1 and a 100 ml flask for cell 2. Approximately 150 ml of 95% ethanol was added for cell 1 and 50 ml for

cell 2, followed by gentle warming on a steam bath to increase the rate of dissolution (2,3). The flasks were placed in a 25.0°C bath, equilibrated, and diluted to the mark. Volumetric flasks were calibrated to contain the desired volume at 25.0°C. Piperidine was weighed out and placed in a 250 ml volumetric flask, 95% ethanol was added, equilibrated at 25.0°C and diluted to the mark with ethanol. The solutions of 2,4-dinitrochlorobenzene were stored in polyethylene stoppered glass reagent bottles. The piperidine solutions were stored in volumetric flasks.

The following general procedure (2,3) was used in making runs. To the cells were added the required volumes of 2,4-dinitrochlorobenzene solution; 30.0 ml to cell 1 and 10.0 ml to cell 2. The cells were equilibrated in a constant temperature bath at the desired temperature. A 10 ml hypodermic syringe containing the appropriate piperidine solution was immersed in the bath for at least 10 minutes. Prior to immersion a small piece of polyethylene tubing was fitted over the tip and shaft of the needle, which prevented water from entering the syringe. The syringe was removed from the water, wiped with an absorbent towel, and carefully injected into the cell to avoid air bubbles, which could cause errors in the first few readings. A stop watch, graduated to one-hundredth of a minute, was started as the cell was injected and readings taken at preset conductances for times less than one minute. For readings of 30 minutes

or less the stop watch was used and a wrist watch for longer times. The reactions were run at 25.0 °C.

The conductance of the 2,4-dinitrochlorobenzene solutions was negligible, as a result, the zero time conductance of the piperidine solutions was used as the conductance at time zero when the reactants were mixed. Time infinity for the reaction was measured after a number of half-lifes, normally 24 to 50 hours after the reaction was run. After following the reaction progress for several half-lifes the reacting mixture was transferred to a flask, sealed and kept in the constant temperature bath from 1 to 2 days at which time the infinity conductances were measured.

On several occasions the formation of large crystals of 2,4-dinitrophenylpiperidine in cell 2 was observed. This phenomena occurred only in cell 2 at concentrations of 0.0020 and 0.0025 mol of 2,4-dinitrochlorobenzene. The large organge crystals which formed on the platinum black surface of the electrodes and the internal cell lead wires appeared to orient in the magnetic field. The crystals were firmly attached to the electrode surface causing trouble in cleaning the cell, several rinsings with warm ethanol were required, and additional time was needed for preparation between runs. Erratic readings for cell 2 at concentrations of 0.0020 and 0.0025 mol/cell volume after several half-lifes necessitated replatinizing the cell. More consistent readings were obtained following

replatinization.

Reactions in dimethylsulfoxide (DMSO). The general procedure used to determine the reaction rate of 2,4-dinitrochlorobenzene in ethanol was used for the reactions in DMSO. However, because of the toxic nature of DMSO and the reactants, precautions were taken to prevent contact with the skin. Polyethylene gloves proved very effective for the work of handling and preparation of solutions.

The conductivity of DMSO (Fischer reagent grade) as received was $7.4 \times 10^{-7}$ ($ohm^{-1}cm^{-1}$). The DMSO was purified by vacuum distillation, under a nitrogen atmosphere with a nitrogen bleed and heated by an IR lamp, from calcium hydride, discarding the first 200 ml of distillate and collecting over molecular sieves (86). The specific conductance of DMSO purified in this manner was $3.0 \times 10^{-7}$ ($ohm^{-1}cm^{-1}$) at 25.0°C. This compares with $0.3 \times 10^{-7}$ ($ohm^{-1}cm^{-1}$) cited in the literature review. An IR spectrum of the distilled DMSO did not exhibit the characteristic O-H bond stretching frequency of water at 3500 $cm^{-1}$.

Eastman Kodak (C.P. grade) piperidine (250 ml) was refluxed with sodium metal for 6 hours to remove water. The piperidine was then distilled from sodium under reduced pressure and collected over molecular sieves (87) rejecting the first 50 ml. The IR spectrum of the distilled piperidine did not display the characteristic O-H stretching band of water at 3500 $cm^{-1}$.

At first several test reactions were run at various concentrations to determine a suitable working concentration range. For cell 1 with 0.0010 mol/cell volume, the reaction proceeded so rapidly, that in the time necessary to make the first measurement the reaction had gone to completion. Solubility of 2,4-dinitrohalobenzenes was no problem, but the faster reaction rate required more dilute solutions than those used by Berkland (3) in order to follow the reaction conveniently. Eventually concentrations of $2.5 \times 10^{-5}$, $5.0 \times 10^{-5}$ and $7.0 \times 10^{-5}$ mol/cell volume were selected. For cell 1 the concentrations were $8.333 \times 10^{-4}$, $1.666 \times 10^{-3}$ and $2.333 \times 10^{-3}$ mol/ℓ. For cell 2, the concentrations corresponded to $2.5 \times 10^{-3}$, $5.0 \times 10^{-3}$, and $7.0 \times 10^{-3}$ mol/ℓ. Piperidine solutions in DMSO were prepared to contain $5.0 \times 10^{-5}$, $1.0 \times 10^{-4}$ and $1.4 \times 10^{-4}$ mol/10 ml. A Chan electrobalance was used to weigh out reagents, since the quantity to be weighed was less than 0.2 g. Piperidine was measured volumetrically by using a 5 ml quantitative buret with an error of ± 0.001 ml.

Solutions of halo-compounds were light yellow in color, but more intense than the ethanol solutions, though less concentrated by a factor of $10^{-2}$. The color of these DMSO solutions appeared to the unaided eye to become more intense over time. A fresh solution was prepared and immediately placed in the conductance cell and the conductance change was monitored. The conductance changed

slowly over a period of several days. The specific conductance for the same number of moles in cell 1 and cell 2 were comparable. Suhr (66) makes no specific reference to the color or stability of the p-nitrochlorobenzene solutions he examined. A solution of p-nitrochlorobenzene in DMSO was prepared. It displayed the same color development as the 2,4-dinitrochlorobenzene compound of this study. A portion of the 2,4-dinitrochlorobenzene solution was diluted with 25 volumes of cold distilled water. The recovered material was dried and had a melting point of 51-52°C. This plus the pale yellow crystalline appearance of the recovered material indicated it was the original reagent 2,4-dinitrochlorobenzene.

Several runs were made with the 2,4-dinitrochlorobenzene in DMSO after the solution had reached a maximum zero conductance value. Reproducible results were obtained. A plot of time versus the log of the conductance for the first few minutes of a run yielded an intercept equivalent to the measured $C_o$, which was the sum of the piperidine and the 2,4-dinitrochlorobenzene in DMSO. Since no secondary reaction products were found that interferred with the principle reaction, the rate studies were performed.

The conductance at zero time is dependent on the concentration of the two reactants. To determine the separate contribution of each reactant, each was placed in cell 1 and cell 2 and diluted to the corresponding cell

volume. The 2,4-dinitrochlorobenzene was found to be the major contributer and the piperidine contribution was minimal. The infinity time conductances were determined after a period of 12 to 24 hours, since the reaction half-life was so short an extremely large number of half-lifes would have occurred during this period of time. Infinity readings were taken on several solutions in order to obtain an average value.

The procedure used to make runs was the same as that described for the ethanol reaction, except that much shorter times were required to reach 80% reaction completion. The time necessary to reach 80% completion ranged from 40 minutes at 25.0°C to 20 minutes at 35.0°C for the 2.5 x $10^{-5}$ mol, 2,4-dinitrochlorobenzene solutions. There was no apparent change in the individual conductance values between runs which could be attributed to the introduction of water or secondary reactions.

Since reproducible measurements were obtained for the chloro-reaction, the bromo and iodo solutions were prepared and reacted following the same procedure at 25.0°C and 35.0°C and the chloro reaction was run at 35.0°C.

Fischer (white label; reagent grade) 2,4-dinitrobromobenzene (DNBB) was dried in a vacuum desiccator and used directly in making the solutions. The actual concentrations used were the same as those listed earlier for the 2,4-dinitrochlorobenzene solutions in DMSO for cell 1 and

cell 2. The piperidine solutions previously prepared for the chloro-reaction were also used for the bromo reactions. The time necessary to reach 80% completion was 30 minutes at 25.0°C and 20 minutes at 35.0°C for the $2.5 \times 10^{-5}$ mol 2,4-dinitrobromobenzene solutions in cell 1. Color development upon making the solutions was similar to that for the chloro-reaction.

Following the improved procedure of Bunnett and Conner (81) 2,4-dinitroiodobenzene was prepared. To 200 ml of N,N-dimethylformamide was added 166.00 g of potassium iodide (1.00 mole) and 40.5 g of 2,4-dinitrochlorobenzene (0.20 mole). This mixture was refluxed with stirring over an open flame for 15 minutes. The hot mixture was poured over ice; the brown precipitate collected and recrystallized three times from 95% ethanol. The yield was 19 g giving a % yield of 32. The mp was 86-87°C compared to 88.5-90°C reported by Bunnett. The mp when recrystallized from ethanol is 88°C (88).

The iodo reactions were run under the same conditions and concentrations as employed for the chloro and bromo analogs. The time necessary to reach 60 to 70% reaction completion was 90 minutes at 25.0°C and 40 minutes at 35.0°C for cell 1. The slower rate of reaction made measurements easier to take than for the chloro and bromo reactions.

## II. Calculations

The reaction velocity or rate of a chemical reaction can be expressed as the rate of change of concentration with time, dC/dt, at a constant temperature, where C is the concentration of the reactant or the product. When defined in this manner, a proportionality exists between the rate and the concentration of the reactants (89).

The reaction rate can be equated to the reactant concentration if a proportionality constant k is multiplied by the product of the reactant concentrations. The proportionality constant k is the reaction rate, specific rate, or rate coefficient when the reactants are at unit concentrations. The dimensions of the rate constant k, are $(mol/\ell)^{1-n}\ sec^{-1}$, where n is the order of the reaction. The order of reaction indicates the manner in which the rate depends on reactant concentration. It is not the same as "molecularity" which concerns the number of molecules entering into an elementary reaction. For example in a second order reaction the rate is proportional to the product of two concentrations. Each concentration can be varied independently and an influence on the rate is observed. Thus the reaction order ($n_t$) is two (c.f. equations 14-17).

$$aA + bB \overset{k}{\rightleftharpoons} cC \tag{14}$$

$$\text{rate} = k[A]^a \times [B]^b \tag{15}$$

$$a = b = 1 \tag{16}$$

$$n_t = a + b = 2 \tag{17}$$

This does not necessarily indicate the number of molecules interacting at some point in the mechanism, though a second order reaction may be bimolecular.

The reaction between 2,4-dinitrohalobenzene and piperidine in 95% ethanol is second order (5). The reaction proceeds in at least two steps (Figure 8), where X represents the halogen substituent.

The rate for this type of reaction can be formulated as:

$$\frac{dx}{dt} = k(a-x)(b-2x) \tag{18}$$

The quantities (a-x) and (b-2x) are the concentrations of the respective reactants at any time t during the reaction. To simplify this calculation, let b = 2a, since two molecules of piperidine take part in the reaction, then the above expression (c.f. equation 18) becomes equation (19),

$$\frac{dx}{dt} = k(a-x)(2a-2x) \tag{19}$$

$$= 2k(a-x)^2 \tag{20}$$

rearrangement of (20) yields (21),

$$\frac{dx}{(a-x)^2} = 2kdt \tag{21}$$

integration of (21) yields (22),

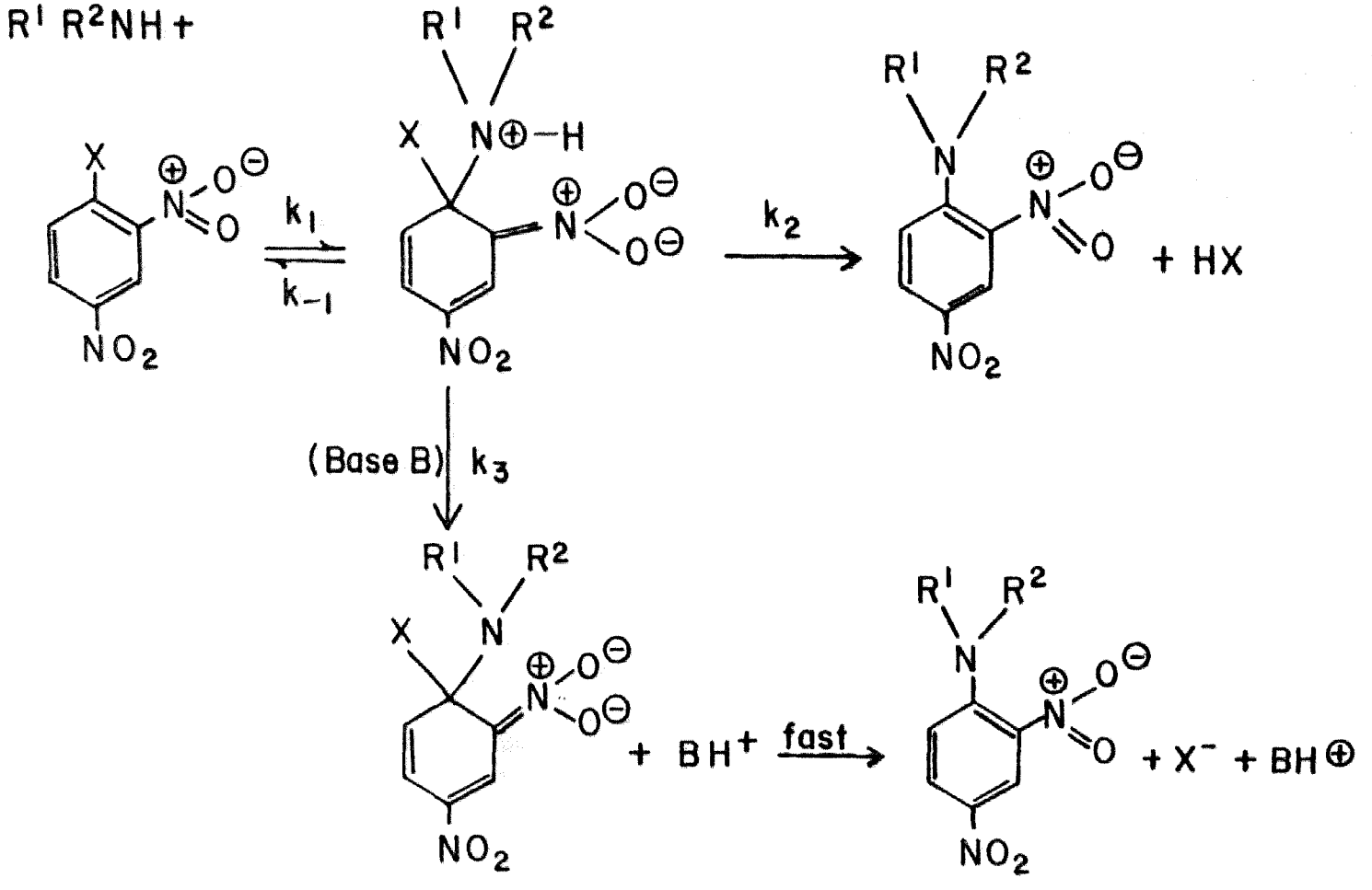



Figure 8. Paths of reaction of 2,4-dinitrohalobenzene with a primary or secondary amine (ref. 90).

$$\frac{1}{(a-x)} = 2kt + \frac{1}{a} \qquad (22)$$

where 1/a is the constant of integration, (t) is the time, a is the initial concentration of 2,4-dinitrohalobenzene, and x is the concentration of either one of the products. Equation (19) is now linear and a plot of the reciprocal of the concentration, 1/(a-x), versus time (t) would yield a straight line with a slope of (2k).

As the reaction in Figure 8 proceeds to completion, the concentration of the reactants decreases and produces an increase in the number of ions in solution. Conductivity can be employed to measure this change in reactant concentration. The conductivity of any solution is dependent upon the amount and type of each ion present. The equivalent conductance ($\Lambda$) represents the conducting power of the ions produced by one gram-equivalent of electrolyte/$\ell$ of solution and can be expressed by equation (23).

$$\Lambda = \frac{1000L}{c} \qquad (23)$$

L is the specific conductance of the ions present and c is the concentration in gram-equivalents/$\ell$ (84). The specific conductance L equals the cell constant K multiplied by the conductance C equation (24). The units for C are $ohm^{-1}cm^{-1}$.

$$L = KC \qquad (24)$$

Combining (23) and (24) yields (25),

$$\frac{\Lambda c}{1000} = KC \tag{25}$$

which can be rewritten as (26)

$$\frac{\Lambda c}{1000K} = C \tag{26}$$

assuming Kohlrausch's law of independent migration of ions at infinite dilution to be applicable to the system of interest (84). Then the equivalent conductance at infinite dilution is due to each ionic species (equation 27) where ($l_c$) and ($l_a$) are the conductance due to the cation and anion respectively (84).

$$\Lambda = l_c + l_a \tag{27}$$

Equation (26) can be written as (28) by using (27),

$$C = \frac{1}{1000K} (c_1 l_1 + c_2 l_2 + c_3 l_3 + --- + c_n l_n) \tag{28}$$

where $C_n$ is the concentration in gram-equivalents/ℓ for each ionic species, (n=1,2,3---),

$l_n$ is the equivalent conductance for each ion (n=1,2,3---),

K is the cell constant, and

C is the total conductance of the solution.

In the reaction between 2,4-dinitrohalobenzene and piperidine, the three conductances in terms of the equivalent conductance of each contributing species that must be determined are:

$$C_o = (a_1 l_1)/1000K, \tag{29}$$

$$C_t = [(2a-2x)_1 l_1 + x_2 l_2 + x_3 l_3 + x_4 l_4]/1000K \tag{30}$$

$$C_\infty = (x_2 l_2 + x_3 l_3 + x_4 l_4)/1000K, \tag{31}$$

where $C_o$ is the conductance of the cell at time zero,

$C_t$ is the conductance of the cell at time t,

$C_\infty$ is the conductance of the cell at equilibrium,

subscript 1 designates the conductance of the piperidine,

subscript 2 designates the conductance of the product 2,4-dinitrophenylpiperidine,

subscript 3 designates the conductance of the product piperidinium ion, and

subscript 4 designates the conductance of the product halide ion.

By subtraction of $C_o$ from both $C_t$ and $C_\infty$ and division of the proper terms, an expression results (equation 32) in which the cell constant and equivalent conductance are eliminated

$$\frac{C_t - C_o}{C_\infty - C_o} = \frac{x}{a} \tag{32}$$

and (x) is the product concentration at time (t) and (a) is the initial concentration of 2,4-dinitrohalobenzene reagent. The ratio $C_t - C_o/C_\infty - C_o$ equates a change in conductance with a change in the substrate, specifically product concentration. This ratio is actually a measure of the percent

reaction completed at time t and multiplying this by the initial concentration a gives the concentration at time t, or the reactant concentration, since the concentration of the remaining reactant (R) is obtained by subtracting the product concentration (P) at time t from 1. Solving equation (32) for x and substituting into equation (22) yields equation (33).

$$\frac{C_\infty - C_o}{C_\infty - C_t} = 2akt + 1 \qquad (33)$$

Equation (33) indicates the reaction rate can be determined through the measurement of the change in a physical property, conductance, with respect to time. Since equation (33) is linear, a plot of the conductance ratio $C_\infty - C_o / C_\infty - C_t$ against time in minutes should yield a straight line with a slope of 2ka and y intercept of 1.

Conductance and time measurements are subject to experimental error. This error is carried over in a plot of the conductance ratio against time (c.f. equation 33). The method of least squares was used to obtain the best straight line parameters through the plotted points (91). The slopes (34), y-intercepts (35), and coefficient of determination, ($r^2$), (36), were calculated for all data.

$$\text{Slope} = 2ka = \frac{n\sum(xy) - \sum x \sum y}{n\sum x - (\sum x)^2} \qquad (34)$$

$$\text{y-intercept} = \frac{\sum(y)\ \sum(x^2) - \sum(xy)\ \sum(x)}{n\sum(x^2) - \sum(x)^2} \qquad (35)$$

$$r^2 = \frac{S\sum y + b\sum xy - n\bar{y}^2}{\sum y^2 - n\bar{y}^2} \qquad (36)$$

In these three equations (x) is the time in minutes, y is the conductance ratio, and (n) is the number of data points. (S) is the slope, usually designated (a) in the straight line equation, and (b) stands for the y-intercept. The coefficient of determination will be smaller than (r), the correlation coefficient. The coefficient of determination (92) is the ratio of the explained variance in ($\dot{y}$), in this case the conductance ratio, divided by the total variance in (y) and therefore provides a truer representation of the unexplained variance.

A computer program (Appendix I) was written to calculate the following: 1) the average conductance $C_t$ at each time for a series of four runs, 2) the standard error, or precision of the mean $C_t$, 3) the 95% confidence interval, 4) the conductance ratio $C_\infty - C_0/C_\infty - C_t$, 5) the slope, y-intercept, coefficient of determination, half-life, reaction rate, and reaction order with respect to time, and 6) the % reaction completed at each measured time.

Variance and the 95% confidence interval were used to express conductance measurement errors for a series of

four runs. The 95% confidence interval is 1.96 times the variance. When used for a small number of observations, ten or less, these two measures provide a more reliable indication of the error than standard deviation which is based on a large sample, in theory infinite (91).

Assuming a normally distributed population, equation (37), where $s_m$ is the variance, S is the standard deviation of the sample, and N is the number of observations, provides an estimate (93) of the deviation of the determined mean from the true population mean. The true population mean will be within a range of $\pm$ 2 $s_m$ of the determined mean 68% of the time.

$$s_m = \frac{S}{\sqrt{N}} \tag{37}$$

In conjunction with this, the 95% confidence interval, equation (38), where the width w is the highest value minus the lowest value in the sample, indicates the true value will lie between the average value $\pm$ $s_w$ with the stated confidence.

$$s_w = w \times k_w \tag{38}$$

The value of $k_w$ for two, three, four, five, and six readings is 0.89, 0.59, 0.49, 0.43, and 0.40 respectively. As the number of readings increases the $k_w$ factor decreases (93).

For measurement times less than one minute, error was expressed as fractions of a minute since pre-set

conductances were used to follow the reaction. These time error measurements were expressed as conductance term variance by calculating the change in the pre-set conductance per change in time (Appendix I).

The half-life of a reaction is the time required for half of a substance to react. By substituting ½a for the concentration term (x) in the integrated rate equation (22) the following equation results:

$$\frac{1}{2ka} = t_{½} = \frac{1}{Slope} \qquad (39)$$

In equation (39) $t_{½}$ represents the time for one half-life period.

As mentioned earlier, molecularity of a reaction and reaction order in terms of the concentrations of the reactants are not necessarily the same. While a determination of reaction order is often done by varying the concentration of one of the reactants and noting the effect on the reaction rate, it is possible to determine the reaction order with respect to time using a single run and measuring the slope at different times corresponding to the reactant concentration. Since the conductance method readily provides the reactant concentration at the measured times, the reaction order with respect to time ($n_t$) was calculated by plotting the $\log_{10}$ of the concentration against the $\log_{10}$ of the velocity. The slope is the order of the reaction (94).

If the temperature range is not too great, the

dependence of the rate constant on temperature is expressed by the emperical Arrhenius equation:

$$\frac{d\ \ln k}{d\ T} = \frac{E_a}{RT^2} \tag{40}$$

where $E_a$ is the activation energy in kcal, T is the absolute temperature in °K, and R is the gas constant. Integration of (40) produces equation (41).

$$\ln k = \frac{-E_a}{RT} + \ln A \tag{41}$$

The A of the integration constant lnA is termed the pre-exponential factor or frequency factor with the same units as the rate constant (94). Converting (41) to common logarithms results in equation (42):

$$\log k = \frac{-E_a}{2.303\ RT} + \log A \tag{42}$$

It follows that for any two rate constants at different temperatures equation (42) can be rewritten as equation (43).

$$\log\left(\frac{k_2}{k_1}\right) = \left(\frac{E_a}{2.303\ R}\right)\left(\frac{T_2-T_1}{T_2T_1}\right) \tag{43}$$

The energy of activation is the added amount of energy required by the reactant molecules to form the activated complex $X^{\pm}$ for a particular reaction. Given the assumption that the activated complex is in equilibrium with the reacting molecules and it decomposes to products at a definite rate, the specific rate for the reaction can be written

as:

$$k = \frac{RT}{Nh} K^{\dagger} \tag{44}$$

where N is Avogardro's number, h is Plancks constant, and $K^{\dagger}$ is the equilibrium constant between the activated state and the reactants. The thermodynamic formulation of reaction rates leads to the following expression:

$$K = \left( e^{\Delta S^{\dagger}/R} \right)\left( e^{-E_a^{\dagger}/RT} \right) \tag{45}$$

where $\Delta S^{\dagger}$ is the entropy change in the system; $E_a^{\dagger}$ is the energy of activation for the activated complex. The combination of equation (44) and (45) yields equation (46).

$$k = \frac{RT}{Nh} \left( e^{\Delta S^{\dagger}/R} \right)\left( e^{-E_a^{\dagger}/RT} \right) \tag{46}$$

Equation (46) after conversion to base 10 logarithms and rearrangement becomes equation (47).

$$\log k = \left( \frac{\Delta S^{\dagger}}{2.303\ R} \right) - \left( \frac{E_a^{\dagger}}{2.303\ RT} \right) + \log \frac{RT}{Nh} \tag{47}$$

In both equation (46) and (47) the $E_a^{\dagger}$ term is the experimentally determined activation energy and (47) may be solved for $\Delta S^{\dagger}$ to determine the change in entropy for the system.

TABLE II

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00100 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .48 | 20.00 | .24[b] | .47 | 1.027 |
| .88 | 33.30 | .16[b] | .33 | 1.066 |
| 1.00 | 37.27 | .91 | 1.81 | 1.078 |
| 2.00 | 64.09 | .48 | 1.12 | 1.168 |
| 3.00 | 85.58 | .40 | .90 | 1.252 |
| 4.00 | 104.36 | .29 | .64 | 1.336 |
| 5.00 | 121.14 | .48 | 1.16 | 1.421 |
| 6.00 | 135.40 | .53 | 1.29 | 1.503 |
| 7.00 | 148.24 | .51 | 1.20 | 1.584 |
| 10.00 | 179.52 | .48 | 1.20 | 1.826 |
| 12.00 | 196.36 | .57 | 1.29 | 1.989 |
| 15.00 | 216.92 | .55 | 1.29 | 2.233 |
| 17.00 | 228.38 | .58 | 1.42 | 2.397 |
| 20.00 | 242.94 | .55 | 1.25 | 2.644 |
| 25.00 | 262.12 | .56 | 1.25 | 3.058 |
| 30.00 | 276.96 | .59 | 1.25 | 3.479 |
| 40.00 | 298.64 | .82 | 1.72 | 4.357 |
| 50.00 | 313.54 | .75 | 1.59 | 5.270 |
| 60.00 | 324.00 | .69 | 1.25 | 6.180 |

[a] $C_o$ = 10.10 Micromhos
$C_\infty$ = 384.60 Micromhos

[b] These values are calculated from errors in time.

TABLE III

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00200 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .40 | 60.00 | 1.29[b] | 2.66 | 1.063 |
| .60 | 80.00 | 1.09[b] | 2.48 | 1.099 |
| 1.00 | 118.55 | 1.28 | 2.84 | 1.177 |
| 2.00 | 194.00 | 1.58 | 3.43 | 1.365 |
| 3.00 | 248.62 | 1.82 | 3.92 | 1.544 |
| 4.00 | 290.47 | 1.95 | 4.21 | 1.717 |
| 5.00 | 324.75 | 2.07 | 4.61 | 1.890 |
| 6.00 | 354.07 | 2.15 | 4.41 | 2.068 |
| 7.00 | 378.32 | 1.16 | 2.65 | 2.243 |
| 10.00 | 431.90 | .70 | 1.47 | 2.758 |
| 12.00 | 458.42 | .70 | 1.42 | 3.112 |
| 15.00 | 487.92 | .72 | 1.52 | 3.630 |
| 17.00 | 503.50 | .76 | 1.62 | 3.980 |
| 20.00 | 522.40 | .65 | 1.22 | 4.507 |
| 25.00 | 545.92 | .77 | 1.57 | 5.397 |
| 30.00 | 563.07 | .78 | 1.62 | 6.304 |
| 40.00 | 585.90 | 1.21 | 2.65 | 8.121 |
| 50.00 | 601.52 | .78 | 1.57 | 10.116 |
| 60.00 | 612.10 | .79 | 1.57 | 12.136 |

[a] $C_o$ = 21.87 Micromhos
$C_\infty$ = 665.10 Micromhos

[b] These values are calculated from errors in time.

TABLE IV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00250 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .27 | 60.00 | 1.16[b] | 2.65 | 1.041 |
| .40 | 80.00 | 1.62[b] | 3.07 | 1.071 |
| .72 | 130.00 | 1.36 | 3.11 | 1.153 |
| 1.00 | 164.25 | 1.44 | 2.94 | 1.218 |
| 2.00 | 261.75 | 1.11 | 2.45 | 1.447 |
| 3.00 | 327.40 | 1.08 | 2.45 | 1.657 |
| 4.00 | 378.35 | 1.14 | 2.40 | 1.868 |
| 5.00 | 419.85 | .59 | 1.37 | 2.084 |
| 6.00 | 452.12 | .96 | 2.25 | 2.290 |
| 7.00 | 478.50 | .82 | 1.96 | 2.490 |
| 10.00 | 537.35 | .67 | 1.52 | 3.097 |
| 12.00 | 565.10 | .63 | 1.42 | 3.498 |
| 15.00 | 596.37 | .56 | 1.22 | 4.097 |
| 17.00 | 612.57 | .48 | 1.13 | 4.496 |
| 20.00 | 632.30 | .47 | 1.13 | 5.100 |
| 25.00 | 656.42 | .57 | 1.22 | 6.101 |
| 30.00 | 673.82 | .66 | 1.37 | 7.111 |
| 40.00 | 697.17 | .69 | 1.47 | 9.138 |
| 50.00 | 712.12 | .72 | 1.52 | 11.177 |
| 60.00 | 722.07 | 1.31 | 2.74 | 13.127 |

[a] $C_o$ = 30.44 Micromhos
$C_\infty$ = 779.10 Micromhos

[b] These values are calculated from errors in time.

TABLE V

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00100 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 at 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .23 | 333.30 | 9.85[b] | 22.29 | 1.029 |
| .38 | 500.00 | 16.23[b] | 38.76 | 1.060 |
| 1.00 | 1060.00 | 10.00 | 19.60 | 1.182 |
| 2.00 | 1732.50 | 7.50 | 14.70 | 1.372 |
| 3.00 | 2203.25 | 8.10 | 16.17 | 1.546 |
| 4.00 | 2570.33 | 10.33 | 20.65 | 1.716 |
| 5.00 | 2876.67 | 9.82 | 18.88 | 1.889 |
| 6.00 | 3127.33 | 8.65 | 17.11 | 2.058 |
| 7.00 | 3335.67 | 6.17 | 12.39 | 2.224 |
| 10.00 | 3813.33 | 8.19 | 16.52 | 2.729 |
| 12.00 | 4042.67 | 7.69 | 15.34 | 3.063 |
| 15.00 | 4306.67 | 6.64 | 13.57 | 3.565 |
| 17.00 | 4444.67 | 6.39 | 12.98 | 3.899 |
| 20.00 | 4612.67 | 7.31 | 14.75 | 4.400 |
| 25.00 | 4822.33 | 5.93 | 11.80 | 5.245 |
| 30.00 | 4976.33 | 5.93 | 11.80 | 6.100 |
| 40.00 | 5184.67 | 6.44 | 12.39 | 7.833 |
| 50.00 | 5324.00 | 4.73 | 9.44 | 9.670 |
| 60.00 | 5411.33 | 6.33 | 12.39 | 11.337 |

[a] $C_o$ = 173.8 Micromhos
$C_\infty$ = 5918.00 Micromhos

[b] These values are calculated from errors in time.

TABLE VI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00200 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .32 | 1250.00 | 42.91[b] | 95.64 | 1.101 |
| .44 | 1666.00 | 42.60[b] | 106.12 | 1.155 |
| 1.00 | 2977.00 | 38.07 | 90.30 | 1.368 |
| 2.00 | 4468.00 | 30.89 | 81.70 | 1.729 |
| 3.00 | 5410.80 | 30.11 | 81.70 | 2.077 |
| 4.00 | 6057.80 | 29.19 | 77.83 | 2.409 |
| 5.00 | 6534.40 | 27.30 | 69.66 | 2.730 |
| 6.00 | 6899.80 | 26.94 | 62.35 | 3.041 |
| 7.00 | 7163.80 | 27.00 | 60.20 | 3.314 |
| 10.00 | 7775.80 | 22.66 | 61.06 | 4.185 |
| 12.00 | 8076.33 | 22.26 | 43.07 | 4.804 |
| 15.00 | 8377.67 | 24.29 | 49.56 | 5.642 |
| 17.00 | 8528.67 | 24.84 | 50.74 | 6.182 |
| 20.00 | 8691.33 | 28.39 | 51.92 | 6.893 |
| 25.00 | 8922.33 | 19.64 | 40.12 | 8.238 |
| 30.00 | 9070.33 | 20.51 | 41.89 | 9.415 |
| 40.00 | 9263.00 | 21.66 | 44.25 | 11.567 |
| 50.00 | 9385.33 | 24.63 | 50.15 | 13.531 |
| 60.00 | 9407.20 | 33.48 | 79.98 | 13.954 |

[a] $C_o$ = 354.8 Micromhos
$C_\infty$ = 10106.00 Micromhos

[b] These values are calculated from errors in time.

TABLE VII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .00250 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 25.0°C IN ETHANOL

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .16 | 1000.00 | 57.84[b] | 102.96 | 1.043 |
| .34 | 2000.00 | 27.03[b] | 48.11 | 1.141 |
| .59 | 3000.00 | 81.63[b] | 145.31 | 1.259 |
| 1.00 | 4296.00 | 104.00 | 185.12 | 1.455 |
| 2.00 | 6120.00 | 120.00 | 213.60 | 1.862 |
| 3.00 | 7204.50 | 129.50 | 230.51 | 2.235 |
| 4.00 | 7920.50 | 133.50 | 237.63 | 2.574 |
| 5.00 | 8432.00 | 133.00 | 236.74 | 2.887 |
| 6.00 | 8822.00 | 133.00 | 236.74 | 3.183 |
| 7.00 | 9126.00 | 129.00 | 229.62 | 3.494 |
| 10.00 | 9746.50 | 126.50 | 225.17 | 4.202 |
| 12.00 | 10116.50 | 21.50 | 38.27 | 4.819 |
| 15.00 | 10294.00 | 130.00 | 231.40 | 5.185 |
| 17.00 | 10435.50 | 127.50 | 226.95 | 5.519 |
| 20.00 | 10601.50 | 127.50 | 226.95 | 5.969 |

[a] $C_o$ = 501.2 Micromhos
$C_\infty$ = 12634.00 Micromhos

[b] These values are calculated from errors in time.

TABLE VIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 at 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .35 | 2.00 | .04[b] | .08 | 1.031 |
| .75 | 3.00 | .06[b] | .12 | 1.103 |
| 1.00 | 3.51 | .06 | .12 | 1.143 |
| 2.00 | 5.33 | .02 | .03 | 1.316 |
| 3.00 | 6.68 | .02 | .03 | 1.484 |
| 4.00 | 7.89 | .04 | .07 | 1.673 |
| 5.00 | 8.82 | .05 | .09 | 1.857 |
| 6.00 | 9.57 | .04 | .07 | 2.037 |
| 7.00 | 10.23 | .04 | .08 | 2.226 |
| 8.00 | 10.77 | .05 | .09 | 2.409 |
| 9.00 | 11.26 | .05 | .08 | 2.601 |
| 10.00 | 11.66 | .03 | .05 | 2.786 |
| 11.00 | 12.04 | .05 | .09 | 2.988 |
| 12.00 | 12.37 | .05 | .09 | 3.185 |
| 13.00 | 12.66 | .05 | .09 | 3.385 |
| 14.00 | 12.93 | .05 | .08 | 3.588 |
| 15.00 | 13.16 | .04 | .08 | 3.792 |
| 20.00 | 14.09 | .04 | .06 | 4.871 |
| 25.00 | 14.67 | .05 | .08 | 5.932 |
| 30.00 | 15.12 | .04 | .08 | 7.149 |

[a] $C_o$ = 1.53 Micromhos
$C_\infty$ = 17.33 Micromhos

[b] These values are calculated from errors in time.

TABLE IX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .28 | 4.00 | .32[b] | .65 | 1.049 |
| .47 | 6.00 | .68[b] | 1.32 | 1.130 |
| 1.00 | 9.21 | .33 | .66 | 1.289 |
| 1.50 | 11.88 | .31 | .57 | 1.461 |
| 2.00 | 13.76 | .29 | .51 | 1.613 |
| 2.50 | 15.55 | .30 | .58 | 1.788 |
| 3.00 | 16.76 | .26 | .49 | 1.930 |
| 3.50 | 18.09 | .25 | .46 | 2.115 |
| 4.00 | 18.92 | .24 | .44 | 2.251 |
| 4.50 | 19.97 | .26 | .50 | 2.448 |
| 5.00 | 20.59 | .24 | .48 | 2.580 |
| 6.00 | 21.86 | .23 | .48 | 3.167 |
| 7.00 | 22.88 | .24 | .48 | 3.230 |
| 8.00 | 23.68 | .25 | .47 | 3.545 |
| 9.00 | 24.46 | .27 | .56 | 3.911 |
| 10.00 | 25.01 | .28 | .55 | 4.224 |
| 15.00 | 26.97 | .30 | .64 | 5.879 |
| 20.00 | 27.81 | .97 | 2.20 | 7.078 |
| 25.00 | 28.20 | .30 | .57 | 7.798 |
| 30.00 | 29.43 | .33 | .58 | 11.585 |

[a] $C_o$ = 2.63 Micromhos
$C_\infty$ = 31.96 Micromhos

[b] These values are calculated from errors in time.

TABLE X

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .26 | 4.00 | .08[b] | .20 | 1.010 |
| .46 | 6.00 | .08[b] | .19 | 1.073 |
| .57 | 8.00 | .22[b] | .46 | 1.144 |
| 1.00 | 12.02 | .20 | .37 | 1.320 |
| 1.50 | 15.09 | .25 | .60 | 1.497 |
| 2.00 | 17.65 | .55 | .98 | 1.684 |
| 2.50 | 20.16 | .35 | .71 | 1.919 |
| 3.00 | 21.95 | .36 | .71 | 2.131 |
| 3.50 | 23.31 | .36 | .66 | 2.327 |
| 4.00 | 24.55 | .39 | .71 | 2.540 |
| 4.50 | 25.38 | .37 | .71 | 2.705 |
| 5.00 | 26.44 | .31 | .55 | 2.950 |
| 6.00 | 27.83 | .42 | .76 | 3.348 |
| 7.00 | 28.94 | .43 | .78 | 3.751 |
| 8.00 | 29.83 | .45 | .81 | 4.153 |
| 9.00 | 30.59 | .50 | .86 | 4.573 |
| 10.00 | 31.19 | .52 | .89 | 4.971 |
| 15.00 | 33.26 | .48 | .84 | 7.077 |
| 20.00 | 34.26 | .48 | .86 | 8.916 |
| 25.00 | 34.93 | .47 | .86 | 10.784 |
| 30.00 | 35.33 | .52 | .95 | 12.377 |

[a] $C_o$ = 3.63 Micromhos
$C_\infty$ = 38.13 Micromhos

[b] These values are calculated from errors in time.

TABLE XI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 35.0°C in DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .22 | 7.00 | .00[b] | .00 | 1.067 |
| .58 | 8.00 | .08[b] | .16 | 1.145 |
| .79 | 8.50 | .02[b] | .04 | 1.189 |
| 1.00 | 9.03 | .09 | .18 | 1.239 |
| 1.50 | 10.03 | .10 | .17 | 1.345 |
| 2.00 | 10.89 | .08 | .15 | 1.453 |
| 2.50 | 11.69 | .11 | .23 | 1.571 |
| 3.00 | 12.38 | .11 | .23 | 1.686 |
| 3.50 | 12.94 | .11 | .22 | 1.795 |
| 4.00 | 13.44 | .11 | .22 | 1.905 |
| 4.50 | 13.87 | .12 | .24 | 2.010 |
| 5.00 | 14.21 | .14 | .27 | 2.103 |
| 6.00 | 14.93 | .10 | .19 | 2.329 |
| 7.00 | 15.57 | .11 | .23 | 2.572 |
| 8.00 | 15.98 | .17 | .35 | 2.760 |
| 9.00 | 16.43 | .14 | .28 | 2.996 |
| 10.00 | 16.79 | .15 | .29 | 3.221 |
| 12.00 | 17.35 | .21 | .42 | 3.639 |
| 15.00 | 18.09 | .15 | .30 | 4.400 |
| 20.00 | 18.88 | .15 | .30 | 5.653 |

[a] $C_o$ = 6.02 Micromhos

$C_\infty$ = 21.64 Micromhos

[b] These values are calculated from errors in time.

TABLE XII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .10 | 14.00 | .63[b] | 1.28 | 1.056 |
| .29 | 16.00 | .18[b] | .31 | 1.138 |
| .50 | 18.00 | .11[b] | .22 | 1.233 |
| 1.00 | 22.03 | .09 | .18 | 1.484 |
| 1.50 | 24.75 | .07 | .14 | 1.719 |
| 2.00 | 26.89 | .05 | .08 | 1.966 |
| 2.50 | 28.67 | .08 | .15 | 2.230 |
| 3.00 | 30.02 | .09 | .18 | 2.486 |
| 3.50 | 31.17 | .10 | .19 | 2.572 |
| 4.00 | 32.15 | .11 | .21 | 3.030 |
| 4.50 | 32.93 | .12 | .24 | 3.296 |
| 5.00 | 33.64 | .11 | .22 | 3.580 |
| 6.00 | 34.79 | .15 | .29 | 4.164 |
| 7.00 | 35.66 | .13 | .24 | 4.743 |
| 8.00 | 36.39 | .12 | .21 | 5.379 |
| 9.00 | 37.07 | .13 | .26 | 6.138 |
| 10.00 | 37.58 | .13 | .25 | 6.870 |

[a] $C_o$ = 12.45 Micromhos
$C_\infty$ = 41.86 Micromhos

[b] These values are calculated from errors in time.

TABLE XIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .05 | 8.00 | .00[b] | .00 | 0.857 |
| .37 | 15.00 | .07[b] | .13 | 1.024 |
| .67 | 20.00 | .05[b] | .10 | 1.191 |
| 1.00 | 24.00 | .00 | .00 | 1.368 |
| 1.50 | 28.03 | .09 | .18 | 1.610 |
| 2.00 | 31.13 | .18 | .37 | 1.861 |
| 2.50 | 33.46 | .21 | .43 | 2.112 |
| 3.00 | 35.31 | .22 | .45 | 2.362 |
| 3.50 | 36.63 | .22 | .44 | 2.583 |
| 4.00 | 37.99 | .21 | .42 | 2.854 |
| 4.50 | 38.95 | .24 | .49 | 3.085 |
| 5.00 | 39.77 | .23 | .48 | 3.314 |
| 6.00 | 41.08 | .23 | .48 | 3.756 |
| 7.00 | 42.09 | .24 | .50 | 4.189 |
| 8.00 | 42.81 | .27 | .55 | 4.564 |
| 9.00 | 43.35 | .29 | .58 | 4.894 |
| 10.00 | 43.88 | .30 | .58 | 5.237 |

[a] $C_o$ = 14.12 Micromhos

$C_\infty$ = 50.86 Micromhos

[b] These values are calculated from errors in time.

TABLE XIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .42 | 50.00 | .59[b] | 1.19 | 1.103 |
| .83 | 80.00 | .63[b] | 1.27 | 1.266 |
| 1.00 | 87.87 | .90 | 1.71 | 1.316 |
| 2.00 | 132.70 | .35 | .65 | 1.708 |
| 3.00 | 161.83 | .58 | 1.06 | 2.117 |
| 4.00 | 182.23 | .34 | .65 | 2.544 |
| 5.00 | 197.37 | .84 | 1.65 | 2.991 |
| 6.00 | 209.27 | .71 | 1.42 | 3.470 |
| 7.00 | 218.47 | .61 | 1.24 | 3.960 |
| 8.00 | 226.03 | .52 | 1.06 | 4.483 |
| 9.00 | 232.43 | .58 | 1.18 | 5.044 |
| 10.00 | 237.27 | .72 | 1.36 | 5.571 |
| 11.00 | 242.26 | .58 | 1.17 | 6.246 |
| 12.00 | 246.13 | .55 | 1.12 | 6.893 |
| 13.00 | 249.57 | .55 | 1.12 | 7.591 |
| 14.00 | 252.53 | .52 | 1.06 | 8.318 |
| 15.00 | 255.13 | .46 | .94 | 9.081 |
| 20.00 | 264.47 | .40 | .77 | 13.539 |
| 25.00 | 270.23 | .37 | .65 | 19.417 |
| 30.00 | 274.01 | .36 | .71 | 27.144 |
| 40.00 | 278.53 | .47 | .91 | 57.795 |

[a] $C_o$ = 25.96 Micromhos
$C_\infty$ = 283.50 Micromhos

[b] These values are calculated from errors in time.

TABLE XV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .29 | 100.00 | 2.11[b] | 4.13 | 1.102 |
| .55 | 160.00 | 1.93[b] | 4.44 | 1.282 |
| 1.00 | 234.65 | .65 | 1.47 | 1.608 |
| 1.50 | 280.10 | 1.07 | 2.18 | 1.903 |
| 2.00 | 321.35 | 1.51 | 3.28 | 2.283 |
| 2.50 | 347.67 | .98 | 1.89 | 2.616 |
| 3.00 | 368.70 | 1.65 | 3.24 | 2.963 |
| 3.50 | 385.93 | 1.79 | 3.54 | 3.322 |
| 4.00 | 400.53 | 1.07 | 2.12 | 3.703 |
| 4.50 | 410.93 | 1.74 | 3.54 | 4.033 |
| 5.00 | 421.27 | 1.29 | 2.99 | 4.424 |
| 6.00 | 436.57 | 1.38 | 3.28 | 5.167 |
| 7.00 | 448.57 | 1.41 | 3.33 | 5.950 |
| 8.00 | 457.95 | 1.41 | 3.33 | 6.748 |
| 9.00 | 465.47 | 1.40 | 3.33 | 7.562 |
| 10.00 | 471.70 | 1.32 | 3.14 | 8.402 |
| 15.00 | 491.40 | 1.54 | 3.63 | 12.950 |
| 20.00 | 501.90 | 1.63 | 3.82 | 18.199 |
| 25.00 | 508.60 | 1.55 | 3.67 | 24.550 |
| 30.00 | 512.90 | 1.60 | 3.82 | 31.635 |

[a] $C_o$ = 56.42 Micromhos
$C_\infty$ = 527.80 Micromhos

[b] These values are calculated from errors in time.

TABLE XVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .26 | 160.00 | 7.99[b] | 16.22 | 1.182 |
| .38 | 200.00 | 4.44[b] | 7.87 | 1.292 |
| .53 | 250.00 | 1.97[b] | 3.34 | 1.462 |
| 1.00 | 354.32 | 3.15 | 6.86 | 2.017 |
| 1.50 | 416.32 | .70 | 1.62 | 2.603 |
| 2.00 | 460.32 | 2.13 | 4.56 | 3.279 |
| 2.50 | 487.50 | 2.50 | 4.45 | 3.905 |
| 3.00 | 515.43 | 1.29 | 2.36 | 4.860 |
| 3.50 | 532.60 | .56 | 1.06 | 5.720 |
| 4.00 | 544.12 | 1.59 | 3.38 | 6.490 |
| 4.50 | 556.37 | 1.53 | 3.38 | 7.574 |
| 5.00 | 564.97 | 1.67 | 3.43 | 8.580 |
| 6.00 | 579.32 | 1.82 | 3.92 | 11.025 |
| 7.00 | 589.35 | 1.75 | 3.63 | 13.763 |
| 8.00 | 596.37 | 1.54 | 3.53 | 16.665 |
| 9.00 | 601.40 | 3.40 | 6.05 | 19.624 |
| 10.00 | 607.90 | 1.60 | 2.85 | 25.476 |
| 15.00 | 617.30 | 4.00 | 7.12 | 44.787 |
| 20.00 | 623.12 | 1.86 | 4.21 | 84.466 |
| 25.00 | 624.00 | 4.20 | 7.48 | 97.432 |
| 30.00 | 625.00 | 3.70 | 6.59 | 118.163 |

[a] $C_o$ = 74.13 Micromhos
$C_\infty$ = 629.70 Micromhos

[b] These values are calculated from errors in time.

TABLE XVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .32 | 120.00 | .00[b] | .00 | 1.116 |
| .54 | 140.00 | 1.54[b] | 2.72 | 1.213 |
| .80 | 160.00 | 2.67[b] | 4.93 | 1.329 |
| 1.00 | 174.33 | 2.19 | 4.13 | 1.426 |
| 1.50 | 197.67 | 2.33 | 4.13 | 1.620 |
| 2.00 | 217.67 | 2.85 | 5.31 | 1.833 |
| 2.50 | 233.17 | 2.59 | 4.72 | 2.041 |
| 3.00 | 246.50 | 2.85 | 5.07 | 2.261 |
| 3.50 | 259.97 | .20 | .41 | 2.539 |
| 4.00 | 268.43 | .72 | 1.36 | 2.750 |
| 4.50 | 275.33 | .94 | 1.83 | 2.952 |
| 5.00 | 283.60 | .40 | .83 | 3.235 |
| 6.00 | 293.50 | .50 | .88 | 3.655 |
| 7.00 | 301.60 | 1.21 | 2.24 | 4.089 |
| 8.00 | 308.00 | 1.71 | 3.19 | 4.512 |
| 9.00 | 313.33 | 1.97 | 3.60 | 4.938 |
| 10.00 | 319.00 | 1.20 | 2.18 | 5.489 |
| 12.00 | 326.57 | 1.10 | 2.12 | 6.479 |
| 15.00 | 334.77 | .95 | 1.83 | 7.960 |
| 20.00 | 344.35 | .35 | .62 | 10.96 |

[a] $C_o$ = 91.10 Micromhos
$C_\infty$ = 369.80 Micromhos

[b] These values are calculated from errors in time.

TABLE XVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .08 | 130.00 | .09[b] | .15 | 0.9426 |
| .31 | 220.00 | 2.65[b] | 4.69 | 1.131 |
| .60 | 300.00 | .92[b] | 1.63 | 1.374 |
| 1.00 | 372.67 | .67 | 1.18 | 1.707 |
| 1.50 | 431.67 | 1.76 | 3.54 | 2.126 |
| 2.00 | 470.67 | .67 | 1.18 | 2.538 |
| 2.50 | 497.13 | 1.17 | 2.30 | 2.921 |
| 3.00 | 518.80 | .78 | 1.59 | 3.334 |
| 3.50 | 535.37 | .99 | 1.95 | 3.738 |
| 4.00 | 548.50 | .92 | 1.77 | 4.136 |
| 4.50 | 559.27 | .68 | 1.30 | 4.530 |
| 5.00 | 568.07 | 1.07 | 2.12 | 4.913 |
| 6.00 | 582.50 | .67 | 1.36 | 5.704 |
| 7.00 | 593.23 | .73 | 1.47 | 6.481 |
| 8.00 | 601.43 | .64 | 1.30 | 7.232 |
| 9.00 | 608.07 | .73 | 1.47 | 7.982 |
| 10.00 | 613.47 | .70 | 1.42 | 8.717 |

[a] $C_o$ = 161.9 Micromhos

$C_\infty$ = 672.10 Micromhos

[b] These values are calculated from errors in time.

TABLE XIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .11 | 150.00 | 3.58[b] | 6.38 | 0.943 |
| .22 | 250.00 | .00[b] | .00 | 1.112 |
| .32 | 300.00 | .00[b] | .00 | 1.222 |
| .65 | 450.00 | 6.94[b] | 13.41 | 1.736 |
| 1.00 | 530.00 | .00 | .00 | 2.237 |
| 1.50 | 604.43 | 1.11 | 2.18 | 3.059 |
| 2.00 | 652.33 | .33 | .59 | 4.005 |
| 2.50 | 682.60 | .80 | 1.47 | 4.979 |
| 3.00 | 704.83 | .73 | 1.47 | 6.061 |
| 3.50 | 721.67 | .60 | 1.18 | 7.256 |
| 4.00 | 735.00 | .50 | .88 | 8.598 |
| 4.50 | 745.27 | .50 | 1.00 | 10.03 |
| 5.00 | 754.03 | .61 | 1.24 | 11.68 |
| 6.00 | 767.67 | .67 | 1.18 | 15.72 |
| 7.00 | 775.37 | .35 | .71 | 19.53 |
| 8.00 | 781.70 | .29 | .59 | 24.40 |
| 9.00 | 786.40 | .23 | .47 | 29.95 |
| 10.00 | 789.87 | .23 | .47 | 35.97 |

[a] $C_o$ = 187.5 Micromhos
$C_\infty$ = 807.10 Micromhos

[b] These values are calculated from errors in time.

TABLE XX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .32 | 1.00 | .01[b] | .01 | 1.032 |
| .60 | 1.50 | .02[b] | .03 | 1.066 |
| 1.00 | 2.19 | .02 | .03 | 1.117 |
| 1.50 | 2.91 | .02 | .04 | 1.175 |
| 2.00 | 3.59 | .03 | .07 | 1.236 |
| 2.50 | 4.20 | .01 | .02 | 1.295 |
| 3.00 | 4.75 | .03 | .06 | 1.354 |
| 3.50 | 5.31 | .00 | .01 | 1.419 |
| 4.00 | 5.75 | .04 | .08 | 1.476 |
| 4.50 | 6.11 | .07 | .15 | 1.526 |
| 5.00 | 6.49 | .07 | .17 | 1.583 |
| 6.00 | 7.28 | .04 | .10 | 1.714 |
| 7.00 | 7.95 | .06 | .12 | 1.843 |
| 8.00 | 8.47 | .05 | .12 | 1.959 |
| 9.00 | 8.93 | .06 | .13 | 2.075 |
| 10.00 | 9.40 | .05 | .13 | 2.205 |
| 15.00 | 11.03 | .06 | .14 | 2.828 |
| 20.00 | 12.07 | .06 | .15 | 3.451 |
| 25.00 | 12.80 | .06 | .15 | 4.076 |
| 30.00 | 13.33 | .07 | .16 | 4.708 |

[a] $C_o$ = 0.48 Micromhos
$C_\infty$ = 16.80 Micromhos

[b] These values are calculated from errors in time.

TABLE XXI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .22 | 2.00 | .02[b] | .04 | 1.036 |
| .35 | 3.00 | .10[b] | .19 | 1.071 |
| .52 | 4.00 | .07[b] | .17 | 1.107 |
| 1.00 | 7.03 | .12 | .26 | 1.235 |
| 1.50 | 9.65 | .05 | .11 | 1.372 |
| 2.00 | 11.63 | .06 | .11 | 1.497 |
| 2.50 | 13.44 | .06 | .15 | 1.633 |
| 3.00 | 14.90 | .10 | .20 | 1.761 |
| 3.50 | 16.18 | .03 | .08 | 1.893 |
| 4.00 | 17.25 | .05 | .11 | 2.020 |
| 5.00 | 19.19 | .03 | .08 | 2.296 |
| 6.00 | 20.76 | .05 | .10 | 2.582 |
| 7.00 | 21.96 | .07 | .15 | 2.854 |
| 8.00 | 22.96 | .07 | .16 | 3.129 |
| 9.00 | 23.82 | .08 | .16 | 3.414 |
| 10.00 | 24.39 | .10 | .22 | 3.630 |
| 15.00 | 26.83 | .14 | .34 | 4.988 |
| 20.00 | 28.53 | .11 | .24 | 6.757 |
| 25.00 | 29.62 | .04 | .09 | 8.727 |
| 30.00 | 30.21 | .06 | .13 | 10.38 |

[a] $C_o$ = 0.87 Micromhos
$C_\infty$ = 33.34 Micromhos

[b] These values are calculated from errors in time.

TABLE XXII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .15 | 2.00 | .17[b] | .30 | 1.018 |
| .22 | 3.00 | .05[b] | .08 | 1.045 |
| .34 | 4.00 | .19[b] | .34 | 1.074 |
| 1.00 | 10.63 | .19 | .35 | 1.316 |
| 1.50 | 13.83 | .09 | .18 | 1.476 |
| 2.00 | 16.20 | .00 | .00 | 1.622 |
| 2.50 | 18.70 | .20 | .35 | 1.811 |
| 3.00 | 20.77 | .18 | .35 | 2.005 |
| 3.50 | 22.31 | .14 | .27 | 2.179 |
| 4.00 | 23.83 | .36 | .67 | 2.381 |
| 4.50 | 24.78 | .16 | .29 | 2.529 |
| 5.00 | 25.81 | .17 | .32 | 2.711 |
| 6.00 | 27.44 | .32 | .66 | 3.060 |
| 7.00 | 28.98 | .24 | .44 | 3.482 |
| 8.00 | 30.11 | .25 | .47 | 3.876 |
| 9.00 | 31.10 | .25 | .47 | 4.303 |
| 10.00 | 31.87 | .27 | .53 | 4.703 |
| 15.00 | 34.53 | .31 | .61 | 6.936 |

[a] $C_o$ = 1.32 Micromhos
$C_\infty$ = 40.12 Micromhos

[b] These values are calculated from errors in time.

TABLE XXIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .38 | 4.00 | .05[b] | .09 | 1.067 |
| .70 | 5.00 | .04[b] | .07 | 1.132 |
| .89 | 5.50 | .01[b] | .02 | 1.167 |
| 1.00 | 5.80 | .00 | .00 | 1.189 |
| 1.50 | 6.85 | .01 | .02 | 1.274 |
| 2.00 | 7.83 | .01 | .02 | 1.366 |
| 2.50 | 8.64 | .03 | .05 | 1.451 |
| 3.00 | 9.40 | .02 | .05 | 1.541 |
| 3.50 | 10.04 | .03 | .05 | 1.627 |
| 4.00 | 10.66 | .03 | .06 | 1.720 |
| 4.50 | 11.19 | .02 | .05 | 1.808 |
| 5.00 | 11.69 | .04 | .07 | 1.899 |
| 6.00 | 12.56 | .04 | .07 | 2.083 |
| 7.00 | 13.27 | .04 | .08 | 2.260 |
| 8.00 | 13.87 | .06 | .12 | 2.437 |
| 9.00 | 14.39 | .06 | .10 | 2.613 |
| 10.00 | 14.87 | .06 | .11 | 2.801 |
| 12.00 | 15.66 | .05 | .10 | 3.178 |
| 15.00 | 16.50 | .06 | .11 | 3.706 |
| 20.00 | 17.55 | .06 | .11 | 4.676 |

[a] $C_o$ = 2.81 Micromhos

$C_\infty$ = 21.56 Micromhos

[b] These values are calculated from errors in time.

TABLE XXIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .16 | 8.00 | .20[b] | .35 | 1.069 |
| .36 | 10.00 | .06[b] | .12 | 1.139 |
| .47 | 11.00 | .03[b] | .06 | 1.177 |
| 1.00 | 15.50 | .00 | .00 | 1.389 |
| 1.50 | 18.60 | .05 | .09 | 1.584 |
| 2.00 | 21.20 | .05 | .09 | 1.797 |
| 2.50 | 23.19 | .04 | .06 | 2.003 |
| 3.00 | 24.83 | .10 | .19 | 2.213 |
| 3.50 | 26.26 | .00 | .01 | 2.433 |
| 4.00 | 27.59 | .04 | .06 | 2.684 |
| 4.50 | 28.61 | .05 | .10 | 2.912 |
| 5.00 | 29.57 | .06 | .11 | 3.166 |
| 6.00 | 31.12 | .04 | .08 | 3.687 |
| 7.00 | 32.35 | .05 | .09 | 4.238 |
| 8.00 | 33.36 | .05 | .11 | 4.835 |
| 9.00 | 34.15 | .05 | .09 | 5.432 |
| 10.00 | 34.79 | .00 | .01 | 6.035 |

[a] $C_o$ = 5.75 Micromhos

$C_\infty$ = 40.56 Micromhos

[b] These values are calculated from errors in time.

TABLE XXV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .18 | 8.00 | .17[b] | .30 | 0.9883 |
| .28 | 10.00 | .13[b] | .24 | 1.036 |
| .49 | 14.00 | .44[b] | .87 | 1.148 |
| 1.00 | 20.43 | .03 | .06 | 1.388 |
| 1.50 | 25.00 | .10 | .18 | 1.631 |
| 2.00 | 28.50 | .12 | .24 | 1.883 |
| 2.50 | 31.45 | .20 | .41 | 2.164 |
| 3.00 | 33.65 | .18 | .35 | 2.435 |
| 3.50 | 35.43 | .19 | .38 | 2.711 |
| 4.00 | 37.17 | .09 | .18 | 3.048 |
| 4.50 | 38.41 | .24 | .47 | 3.346 |
| 5.00 | 39.84 | .12 | .23 | 3.767 |
| 6.00 | 41.31 | .21 | .41 | 4.332 |
| 7.00 | 42.72 | .22 | .43 | 5.056 |
| 8.00 | 43.85 | .23 | .45 | 5.832 |
| 9.00 | 44.75 | .26 | .51 | 6.654 |
| 10.00 | 45.45 | .27 | .55 | 7.465 |

[a] $C_o$ = 8.51 Micromhos

$C_\infty$ = 51.16 Micromhos

[b] These values are calculated from errors in time.

TABLE XXVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .25 | 25.00 | .68[b] | 1.20 | 1.054 |
| .60 | 50.00 | .62[b] | 1.25 | 1.157 |
| 1.00 | 73.67 | .33 | .59 | 1.275 |
| 1.50 | 97.33 | .67 | 1.18 | 1.421 |
| 2.00 | 117.63 | .71 | 1.42 | 1.576 |
| 2.50 | 133.60 | .23 | .47 | 1.723 |
| 3.00 | 146.27 | 1.11 | 2.24 | 1.861 |
| 3.50 | 159.57 | .47 | .88 | 2.032 |
| 4.00 | 170.90 | .38 | .77 | 2.204 |
| 4.50 | 179.27 | .37 | .71 | 2.352 |
| 5.00 | 189.00 | .58 | 1.18 | 2.550 |
| 6.00 | 201.70 | .56 | 1.06 | 2.865 |
| 7.00 | 212.83 | .12 | .24 | 3.213 |
| 8.00 | 222.80 | .36 | .71 | 3.607 |
| 9.00 | 230.40 | .50 | .88 | 3.977 |
| 10.00 | 237.40 | .56 | 1.06 | 4.392 |
| 15.00 | 260.17 | .47 | .88 | 6.652 |
| 20.00 | 273.13 | .44 | .83 | 9.412 |
| 25.00 | 280.73 | .73 | 1.47 | 12.43 |
| 30.00 | 286.17 | .69 | 1.36 | 16.14 |

[a] $C_o$ = 10.23 Micromhos
$C_\infty$ = 304.40 Micromhos

[b] These values are calculated from errors in time.

TABLE XXVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .17 | 50.00 | .88 [b] | 1.56 | 1.055 |
| .36 | 100.00 | 1.75 [b] | 3.11 | 1.165 |
| .61 | 150.00 | .67 [b] | 1.18 | 1.300 |
| 1.00 | 211.40 | .70 | 1.30 | 1.516 |
| 1.50 | 271.33 | 1.76 | 3.54 | 1.810 |
| 2.00 | 309.65 | 1.35 | 2.40 | 2.065 |
| 2.50 | 345.33 | 1.67 | 2.95 | 2.379 |
| 3.00 | 369.77 | 1.13 | 2.18 | 2.653 |
| 3.50 | 391.00 | 1.00 | 1.77 | 2.951 |
| 4.00 | 409.00 | .76 | 1.47 | 3.261 |
| 5.00 | 435.83 | .93 | 1.77 | 3.864 |
| 6.00 | 458.60 | 1.23 | 2.48 | 4.585 |
| 7.00 | 474.47 | 1.24 | 2.54 | 5.270 |
| 8.00 | 487.83 | 1.35 | 2.71 | 6.027 |
| 9.00 | 497.30 | 1.70 | 3.03 | 6.711 |
| 10.00 | 504.30 | 2.40 | 4.90 | 7.326 |
| 15.00 | 536.50 | 1.75 | 3.19 | 12.66 |
| 20.00 | 551.70 | 1.90 | 3.42 | 19.29 |
| 25.00 | 561.23 | 2.19 | 4.19 | 28.72 |
| 30.00 | 567.17 | 2.03 | 3.66 | 41.28 |

[a] $C_o$ = 20.89 Micromhos
$C_\infty$ = 580.73 Micromhos

[b] These values are calculated from errors in time.

TABLE XXVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .12 | 50.00 | .00[b] | .00 | 1.028 |
| .22 | 100.00 | .00[b] | .00 | 1.112 |
| .37 | 150.00 | .00[b] | .00 | 1.213 |
| 1.00 | 301.00 | 1.00 | 1.77 | 1.663 |
| 1.50 | 374.67 | .33 | .59 | 2.032 |
| 2.00 | 429.67 | .33 | .59 | 2.436 |
| 2.50 | 468.13 | .87 | 1.53 | 2.828 |
| 3.00 | 500.40 | 1.21 | 2.30 | 3.269 |
| 3.50 | 523.30 | 1.18 | 2.30 | 3.677 |
| 4.00 | 544.33 | 1.20 | 2.36 | 4.152 |
| 4.50 | 560.47 | 1.25 | 2.36 | 4.609 |
| 6.00 | 596.50 | 1.26 | 2.36 | 6.112 |
| 7.00 | 614.67 | .88 | 1.77 | 7.315 |
| 8.00 | 628.30 | 1.01 | 1.95 | 8.582 |
| 9.00 | 639.00 | .76 | 1.47 | 9.932 |
| 10.00 | 647.67 | .77 | 1.53 | 11.38 |
| 15.00 | 674.13 | 1.40 | 2.71 | 20.55 |

[a] $C_o$ = 31.60 Micromhos

$C_\infty$ = 707.00 Micromhos

[b] These values are calculated from errors in time.

TABLE XXIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .34 | 80.00 | 1.11[b] | 1.96 | 1.115 |
| .50 | 100.00 | .00[b] | .00 | 1.192 |
| .72 | 120.00 | .00[b] | .00 | 1.280 |
| 1.00 | 141.67 | .33 | .59 | 1.391 |
| 1.50 | 173.50 | .50 | .88 | 1.595 |
| 2.00 | 198.50 | 1.32 | 2.65 | 1.803 |
| 2.50 | 221.17 | .93 | 1.77 | 2.044 |
| 3.00 | 235.83 | 1.36 | 2.65 | 2.239 |
| 3.50 | 250.67 | .67 | 1.18 | 2.476 |
| 4.00 | 262.47 | .84 | 1.65 | 2.705 |
| 4.50 | 274.20 | 1.73 | 3.54 | 2.977 |
| 5.00 | 281.67 | .97 | 1.95 | 3.182 |
| 6.00 | 297.07 | 1.48 | 2.83 | 3.708 |
| 7.00 | 308.23 | 1.19 | 2.36 | 4.211 |
| 8.00 | 317.40 | 1.17 | 2.36 | 4.740 |
| 9.00 | 325.23 | 1.21 | 2.48 | 5.309 |
| 10.00 | 331.50 | 1.16 | 2.36 | 5.874 |
| 12.00 | 341.53 | 1.16 | 2.36 | 7.079 |
| 15.00 | 352.23 | 1.10 | 2.24 | 9.064 |
| 20.00 | 363.07 | 1.07 | 2.18 | 12.65 |

[a] $C_o$ = 44.26 Micromhos

$C_\infty$ = 390.42 Micromhos

[b] These values are calculated from errors in time.

TABLE XXX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .27 | 160.00 | 2.89[b] | 5.79 | 1.128 |
| .39 | 200.00 | 3.24[b] | 5.74 | 1.213 |
| .54 | 240.00 | .87[b] | 1.54 | 1.312 |
| 1.00 | 334.67 | 1.76 | 3.54 | 1.624 |
| 1.50 | 402.33 | 1.20 | 2.36 | 1.959 |
| 2.00 | 451.00 | 1.53 | 2.95 | 2.299 |
| 2.50 | 485.00 | 1.53 | 2.95 | 2.616 |
| 3.00 | 514.13 | 1.34 | 2.60 | 2.968 |
| 3.50 | 536.13 | 1.43 | 2.89 | 3.302 |
| 4.00 | 554.33 | 1.59 | 3.24 | 3.642 |
| 4.50 | 569.07 | 1.74 | 3.54 | 3.973 |
| 5.00 | 582.03 | 1.74 | 3.54 | 4.317 |
| 6.00 | 602.03 | 1.39 | 2.83 | 4.985 |
| 7.00 | 617.53 | 1.82 | 3.72 | 5.664 |
| 8.00 | 629.60 | 1.93 | 3.95 | 6.337 |
| 9.00 | 639.37 | 1.82 | 3.72 | 7.010 |
| 10.00 | 647.33 | 1.88 | 3.83 | 7.724 |

[a] $C_o$ = 87.10 Micromhos
$C_\infty$ = 731.30 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROBROMOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .18 | 180.00 | 4.04[b] | 7.16 | 1.077 |
| .27 | 220.00 | .00[b] | .00 | 1.141 |
| .33 | 260.00 | 6.67[b] | 11.80 | 1.214 |
| 1.00 | 486.67 | 1.67 | 2.95 | 1.904 |
| 1.50 | 580.67 | .67 | 1.18 | 2.491 |
| 2.00 | 641.37 | .68 | 1.24 | 3.110 |
| 2.50 | 682.70 | 3.39 | 6.49 | 3.744 |
| 3.00 | 715.03 | 3.53 | 6.49 | 4.453 |
| 3.50 | 740.37 | 3.72 | 7.08 | 5.230 |
| 4.00 | 760.27 | 4.54 | 8.67 | 6.061 |
| 4.50 | 776.60 | 4.67 | 8.67 | 6.969 |
| 5.00 | 791.27 | 4.01 | 7.49 | 8.052 |
| 6.00 | 812.07 | 5.48 | 10.56 | 10.33 |
| 7.00 | 827.30 | 5.60 | 10.56 | 13.03 |
| 8.00 | 839.37 | 6.03 | 11.39 | 16.43 |
| 9.00 | 849.23 | 6.17 | 11.62 | 20.89 |
| 10.00 | 857.00 | 6.57 | 12.51 | 26.56 |

[a] $C_o$ = 125.9 Micromhos
$C_\infty$ = 885.60 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .50 | .70 | .00[b] | .00 | 1.013 |
| 1.00 | .80 | .10 | .17 | 1.020 |
| 2.00 | 1.19 | .08 | .14 | 1.046 |
| 3.00 | 1.55 | .08 | .14 | 1.071 |
| 4.00 | 1.89 | .08 | .14 | 1.096 |
| 5.00 | 2.21 | .07 | .13 | 1.120 |
| 6.00 | 2.51 | .07 | .13 | 1.145 |
| 7.00 | 2.81 | .07 | .12 | 1.170 |
| 8.00 | 3.09 | .07 | .12 | 1.194 |
| 9.00 | 3.36 | .07 | .13 | 1.219 |
| 10.00 | 3.63 | .07 | .12 | 1.245 |
| 11.00 | 3.87 | .07 | .12 | 1.269 |
| 12.00 | 4.01 | .01 | .02 | 1.283 |
| 13.00 | 4.26 | .04 | .09 | 1.310 |
| 14.00 | 4.49 | .04 | .08 | 1.335 |
| 15.00 | 4.70 | .04 | .08 | 1.358 |
| 20.00 | 5.68 | .05 | .11 | 1.483 |
| 30.00 | 7.20 | .09 | .18 | 1.727 |
| 60.00 | 10.13 | .04 | .08 | 2.530 |
| 90.00 | 11.71 | .03 | .06 | 3.373 |

[a] $C_o$ = 0.50 Micromhos
$C_\infty$ = 16.43 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .42 | 1.40 | .01[b] | .01 | 1.020 |
| 1.00 | 2.23 | .02 | .04 | 1.048 |
| 2.00 | 3.58 | .04 | .10 | 1.097 |
| 3.00 | 4.80 | .09 | .20 | 1.145 |
| 4.00 | 5.98 | .10 | .21 | 1.196 |
| 5.00 | 6.99 | .14 | .30 | 1.243 |
| 6.00 | 7.99 | .12 | .27 | 1.294 |
| 7.00 | 8.90 | .14 | .31 | 1.344 |
| 8.00 | 9.74 | .16 | .35 | 1.394 |
| 9.00 | 10.52 | .17 | .37 | 1.443 |
| 10.00 | 11.25 | .18 | .40 | 1.493 |
| 11.00 | 11.95 | .20 | .46 | 1.544 |
| 12.00 | 12.60 | .22 | .50 | 1.594 |
| 13.00 | 13.19 | .23 | .50 | 1.643 |
| 14.00 | 13.74 | .23 | .50 | 1.691 |
| 15.00 | 14.29 | .25 | .56 | 1.743 |
| 20.00 | 16.34 | .26 | .57 | 1.964 |
| 25.00 | 18.39 | .37 | .81 | 2.249 |
| 30.00 | 19.74 | .40 | .93 | 2.487 |

[a] $C_o$ = 0.78 Micromhos
$C_\infty$ = 32.49 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .17 | 1.40 | .00[b] | .00 | 1.008 |
| .59 | 2.50 | .03[b] | .05 | 1.036 |
| 1.00 | 3.47 | .05 | .09 | 1.061 |
| 1.50 | 4.52 | .01 | .02 | 1.090 |
| 2.00 | 5.68 | .04 | .09 | 1.124 |
| 2.50 | 6.74 | .13 | .25 | 1.157 |
| 3.00 | 7.88 | .06 | .12 | 1.194 |
| 3.50 | 8.76 | .11 | .23 | 1.225 |
| 4.00 | 9.63 | .14 | .29 | 1.257 |
| 4.50 | 10.48 | .12 | .25 | 1.290 |
| 5.00 | 11.30 | .13 | .25 | 1.323 |
| 6.00 | 12.77 | .17 | .34 | 1.387 |
| 7.00 | 14.31 | .27 | .53 | 1.462 |
| 8.00 | 15.55 | .13 | .24 | 1.528 |
| 9.00 | 16.63 | .19 | .34 | 1.590 |
| 10.00 | 17.81 | .13 | .24 | 1.665 |
| 12.00 | 19.77 | .16 | .28 | 1.805 |
| 15.00 | 22.15 | .15 | .27 | 2.012 |
| 20.00 | 25.29 | .17 | .29 | 2.338 |
| 25.00 | 27.64 | .20 | .35 | 2.730 |
| 30.00 | 29.32 | .37 | .67 | 3.065 |

[a] $C_o$ = 1.050 Micromhos
$C_\infty$ = 43.01 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .49 | 1.50 | .00[b] | .01 | 1.014 |
| 1.00 | 1.88 | .01 | .02 | 1.035 |
| 1.50 | 2.20 | .01 | .01 | 1.053 |
| 2.00 | 2.54 | .01 | .02 | 1.074 |
| 2.50 | 2.87 | .02 | .04 | 1.094 |
| 3.00 | 3.19 | .01 | .02 | 1.115 |
| 3.50 | 3.46 | .00 | .00 | 1.133 |
| 4.00 | 3.74 | .00 | .01 | 1.154 |
| 4.50 | 4.01 | .01 | .01 | 1.173 |
| 5.00 | 4.25 | .01 | .02 | 1.199 |
| 6.00 | 4.76 | .02 | .04 | 1.231 |
| 7.00 | 5.18 | .02 | .03 | 1.266 |
| 8.00 | 5.66 | .03 | .06 | 1.309 |
| 9.00 | 6.10 | .03 | .05 | 1.350 |
| 10.00 | 6.43 | .07 | .14 | 1.383 |
| 15.00 | 8.24 | .02 | .04 | 1.597 |
| 20.00 | 9.59 | .02 | .05 | 1.807 |
| 25.00 | 10.66 | .05 | .10 | 2.014 |
| 30.00 | 11.58 | .07 | .14 | 2.236 |
| 40.00 | 12.99 | .05 | .09 | 2.692 |

[a] $C_o$ = 1.25 Micromhos
$C_\infty$ = 19.93 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .56 | 3.00 | .00[b] | .00 | 1.035 |
| 1.00 | 4.17 | .03 | .06 | 1.068 |
| 1.50 | 5.30 | .00 | .00 | 1.104 |
| 2.00 | 6.25 | .05 | .09 | 1.136 |
| 2.50 | 7.51 | .03 | .05 | 1.180 |
| 3.00 | 8.48 | .02 | .03 | 1.217 |
| 3.50 | 9.43 | .02 | .04 | 1.256 |
| 4.00 | 10.31 | .02 | .04 | 1.294 |
| 4.50 | 11.18 | .02 | .03 | 1.333 |
| 5.00 | 11.95 | .04 | .07 | 1.371 |
| 6.00 | 13.39 | .03 | .06 | 1.447 |
| 7.00 | 14.70 | .05 | .09 | 1.524 |
| 8.00 | 15.91 | .04 | .06 | 1.602 |
| 9.00 | 17.00 | .05 | .09 | 1.680 |
| 10.00 | 17.98 | .04 | .08 | 1.757 |
| 11.00 | 18.93 | .07 | .12 | 1.838 |
| 12.00 | 19.75 | .04 | .08 | 1.915 |
| 13.00 | 20.55 | .05 | .08 | 1.996 |
| 14.00 | 21.29 | .05 | .08 | 2.077 |
| 15.00 | 21.96 | .03 | .06 | 2.157 |
| 20.00 | 24.66 | .04 | .07 | 2.550 |

[a] $C_o$ = 1.75 Micromhos
$C_\infty$ = 39.43 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 1 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$. | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .27 | 3.00 | .00[b] | .00 | 1.020 |
| .37 | 3.50 | .00[b] | .00 | 1.031 |
| .54 | 4.00 | .05[b] | .09 | 1.042 |
| 1.00 | 5.97 | .24 | .47 | 1.087 |
| 1.50 | 8.36 | .04 | .08 | 1.148 |
| 2.00 | 10.24 | .02 | .04 | 1.201 |
| 2.50 | 11.96 | .04 | .07 | 1.254 |
| 3.00 | 13.44 | .10 | .21 | 1.303 |
| 3.50 | 15.19 | .09 | .15 | 1.367 |
| 4.00 | 16.19 | .17 | .34 | 1.406 |
| 4.50 | 17.64 | .12 | .20 | 1.468 |
| 5.00 | 18.71 | .14 | .29 | 1.516 |
| 6.00 | 20.88 | .14 | .29 | 1.625 |
| 7.00 | 22.84 | .13 | .25 | 1.738 |
| 8.00 | 24.57 | .11 | .21 | 1.852 |
| 9.00 | 25.95 | .20 | .41 | 1.953 |
| 10.00 | 27.30 | .22 | .45 | 2.065 |
| 11.00 | 28.56 | .20 | .41 | 2.181 |
| 12.00 | 29.64 | .19 | .39 | 2.290 |
| 13.00 | 30.68 | .19 | .40 | 2.408 |
| 14.00 | 31.65 | .20 | .41 | 2.528 |
| 15.00 | 32.49 | .22 | .45 | 2.642 |
| 20.00 | 35.83 | .29 | .59 | 3.224 |

[a] $C_o$ = 2.04 Micromhos
$C_\infty$ = 51.03 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .52 | 15.00 | .04[b] | .07 | 1.023 |
| 1.00 | 21.40 | .21 | .41 | 1.047 |
| 2.00 | 33.42 | .09 | .16 | 1.094 |
| 3.00 | 44.48 | .02 | .03 | 1.142 |
| 4.00 | 54.43 | .02 | .03 | 1.188 |
| 5.00 | 64.13 | .19 | .35 | 1.238 |
| 6.00 | 73.02 | .18 | .32 | 1.287 |
| 7.00 | 81.03 | .17 | .35 | 1.334 |
| 8.00 | 88.55 | .11 | .23 | 1.382 |
| 9.00 | 95.87 | .33 | .66 | 1.432 |
| 10.00 | 102.20 | .06 | .12 | 1.479 |
| 11.00 | 108.33 | .12 | .24 | 1.526 |
| 12.00 | 114.42 | .13 | .27 | 1.577 |
| 13.00 | 119.90 | .10 | .18 | 1.627 |
| 14.00 | 125.23 | .03 | .06 | 1.677 |
| 15.00 | 129.90 | .20 | .35 | 1.723 |
| 20.00 | 151.00 | .10 | .18 | 1.971 |
| 30.00 | 180.77 | .38 | .77 | 2.472 |
| 60.00 | 226.87 | .29 | .59 | 4.082 |
| 90.00 | 248.10 | .15 | .29 | 5.848 |

[a] $C_o$ = 8.51 Micromhos
$C_\infty$ = 297.70 Micromhos

[b] These values are calculated from errors in time.

TABLE XXXIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .40 | 30.00 | 1.20[b] | 2.56 | 1.030 |
| 1.00 | 62.60 | .80 | 1.47 | 1.093 |
| 2.00 | 108.67 | .44 | .88 | 1.197 |
| 3.00 | 145.30 | .60 | 1.06 | 1.293 |
| 4.00 | 178.40 | .86 | 1.65 | 1.396 |
| 5.00 | 207.22 | .89 | 1.76 | 1.499 |
| 6.00 | 229.25 | 1.48 | 2.94 | 1.589 |
| 7.00 | 253.00 | .76 | 1.47 | 1.700 |
| 8.00 | 273.47 | 1.55 | 3.01 | 1.807 |
| 9.00 | 290.40 | 1.07 | 2.06 | 1.907 |
| 10.00 | 305.73 | 1.13 | 2.06 | 2.007 |
| 11.00 | 319.53 | .53 | .94 | 2.108 |
| 12.00 | 333.67 | .99 | 2.01 | 2.222 |
| 13.00 | 345.73 | 1.05 | 2.12 | 2.328 |
| 14.00 | 356.63 | 1.07 | 2.18 | 2.434 |
| 15.00 | 366.63 | 1.06 | 2.06 | 2.540 |
| 20.00 | 407.93 | 1.16 | 2.36 | 3.097 |
| 25.00 | 436.67 | 1.04 | 2.12 | 3.654 |
| 30.00 | 459.00 | .95 | 1.89 | 4.252 |

[a] $C_o$ = 12.88 Micromhos
$C_\infty$ = 596.30 Micromhos

[b] These values are calculated from errors in time.

TABLE XL

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 25.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .21 | 30.00 | .31[b] | .60 | 1.018 |
| .53 | 60.00 | .55[b] | .93 | 1.060 |
| 1.00 | 98.50 | 2.18 | 4.41 | 1.121 |
| 1.50 | 134.00 | 2.61 | 4.90 | 1.183 |
| 2.00 | 167.50 | 3.40 | 6.61 | 1.248 |
| 2.50 | 196.75 | 3.98 | 7.59 | 1.311 |
| 3.00 | 224.12 | 4.25 | 9.06 | 1.376 |
| 3.50 | 246.25 | 4.93 | 10.04 | 1.433 |
| 4.00 | 268.50 | 5.58 | 11.02 | 1.496 |
| 4.50 | 289.37 | 5.48 | 10.53 | 1.560 |
| 5.00 | 308.12 | 6.26 | 12.49 | 1.623 |
| 6.00 | 346.20 | 6.76 | 13.96 | 1.766 |
| 7.00 | 376.27 | 6.78 | 13.96 | 1.899 |
| 8.00 | 407.00 | 2.02 | 4.13 | 2.058 |
| 9.00 | 430.72 | 3.89 | 9.02 | 2.199 |
| 10.00 | 452.62 | .79 | 1.86 | 2.348 |
| 12.00 | 488.70 | 1.24 | 2.55 | 2.643 |
| 15.00 | 528.87 | .94 | 1.77 | 3.073 |
| 20.00 | 574.75 | .75 | 1.33 | 3.774 |
| 25.00 | 609.45 | 2.25 | 4.00 | 4.560 |
| 30.00 | 634.40 | 2.30 | 4.09 | 5.364 |

[a] $C_o$ = 16.85 Micromhos
$C_\infty$ = 775.90 Micromhos

[b] These values are calculated from errors in time.

TABLE XLI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000025 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .29 | 25.00 | .16[b] | .29 | 1.016 |
| .50 | 30.00 | .00[b] | .00 | 1.031 |
| 1.00 | 41.47 | .09 | .18 | 1.067 |
| 1.50 | 52.07 | .07 | .12 | 1.101 |
| 2.00 | 61.63 | .19 | .35 | 1.136 |
| 2.50 | 71.23 | .19 | .35 | 1.172 |
| 3.00 | 80.27 | .37 | .71 | 1.209 |
| 3.50 | 88.33 | .33 | .59 | 1.244 |
| 4.00 | 96.10 | .49 | 1.00 | 1.277 |
| 4.50 | 103.50 | .29 | .59 | 1.314 |
| 5.00 | 110.63 | .35 | .71 | 1.350 |
| 6.00 | 123.40 | .31 | .59 | 1.421 |
| 7.00 | 134.53 | .18 | .35 | 1.488 |
| 8.00 | 145.17 | .17 | .29 | 1.588 |
| 9.00 | 155.63 | .45 | .88 | 1.634 |
| 10.00 | 164.53 | .39 | .77 | 1.704 |
| 12.00 | 181.10 | .59 | 1.18 | 1.854 |
| 15.00 | 200.73 | .80 | 1.53 | 2.070 |
| 20.00 | 225.80 | .49 | 1.00 | 2.429 |
| 25.00 | 244.40 | .21 | .41 | 2.788 |
| 30.00 | 259.20 | .47 | .94 | 3.160 |
| 40.00 | 280.07 | .61 | 1.24 | 3.892 |

[a] $C_o$ = 19.50 Micromhos
$C_\infty$ = 370.10 Micromhos

[b] These values are calculated from errors in time.

TABLE XLII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000050 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .27 | 40.00 | .86[b] | 1.52 | 1.024 |
| .48 | 60.00 | .00[b] | .00 | 1.055 |
| 1.00 | 104.40 | .40 | .71 | 1.131 |
| 1.50 | 142.73 | .27 | .47 | 1.206 |
| 2.00 | 175.90 | .56 | 1.06 | 1.280 |
| 2.50 | 205.50 | .50 | .88 | 1.354 |
| 3.00 | 230.27 | .15 | .29 | 1.423 |
| 3.50 | 254.93 | .23 | .47 | 1.498 |
| 4.00 | 276.60 | .21 | .41 | 1.572 |
| 4.50 | 297.27 | .15 | .29 | 1.649 |
| 5.00 | 314.33 | .17 | .29 | 1.719 |
| 6.00 | 346.83 | .60 | 1.18 | 1.868 |
| 7.00 | 373.97 | .37 | .71 | 2.016 |
| 8.00 | 399.03 | .48 | .88 | 2.174 |
| 9.00 | 418.63 | .41 | .83 | 2.315 |
| 10.00 | 436.20 | .61 | 1.18 | 2.460 |
| 11.00 | 452.57 | .35 | .71 | 2.611 |
| 12.00 | 467.07 | .47 | .88 | 2.761 |
| 13.00 | 480.03 | .29 | .59 | 2.911 |
| 14.00 | 491.90 | .21 | .41 | 3.064 |
| 15.00 | 502.00 | .29 | .59 | 3.206 |
| 20.00 | 543.50 | .29 | .59 | 3.966 |

[a] $C_o$ = 23.44 Micromhos
$C_\infty$ = 718.70 Micromhos

[b] These values are calculated from errors in time.

TABLE XLIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .000070 MOLES OF 2,4-DINITROIODOBENZENE IN CELL 2 AT 35.0°C IN DIMETHYL SULFOXIDE

| Time (t) in min | Average $C_t$ in Micromhos | $\frac{S}{\sqrt{N}}$ | 95 Percent Confidence Interval | $\frac{C_\infty - C_o}{C_\infty - C_t}$ [a] |
|---|---|---|---|---|
| .17 | 50.00 | .00[b] | .00 | 1.022 |
| .34 | 80.00 | .00[b] | .00 | 1.059 |
| .47 | 100.00 | .00[b] | .00 | 1.085 |
| 1.00 | 176.00 | 2.00 | 3.54 | 1.197 |
| 1.50 | 232.67 | .33 | .59 | 1.297 |
| 2.00 | 283.33 | .88 | 1.77 | 1.401 |
| 2.50 | 333.00 | 3.51 | 6.49 | 1.520 |
| 3.00 | 363.67 | .88 | 1.77 | 1.606 |
| 3.50 | 397.67 | 1.86 | 3.54 | 1.712 |
| 4.00 | 430.67 | 1.33 | 2.36 | 1.829 |
| 4.50 | 455.33 | 1.86 | 3.54 | 1.928 |
| 5.00 | 479.33 | 1.45 | 2.95 | 2.034 |
| 6.00 | 514.83 | 6.82 | 13.27 | 2.217 |
| 7.00 | 557.60 | 1.80 | 3.24 | 2.484 |
| 8.00 | 587.30 | 1.33 | 2.71 | 2.711 |
| 9.00 | 613.40 | 1.42 | 2.89 | 2.949 |
| 10.00 | 634.57 | 1.95 | 3.95 | 3.174 |
| 11.00 | 654.20 | 1.74 | 3.54 | 3.416 |
| 12.00 | 672.40 | 2.60 | 5.31 | 3.674 |
| 13.00 | 686.67 | 2.03 | 4.13 | 3.907 |
| 14.00 | 700.43 | 1.89 | 3.83 | 4.161 |
| 15.00 | 711.00 | 2.00 | 3.56 | 4.380 |
| 20.00 | 759.77 | 2.38 | 4.31 | 5.782 |

[a] $C_o$ = 31.23 Micromhos

$C_\infty$ = 912.10 Micromhos

[b] These values are calculated from errors in time.

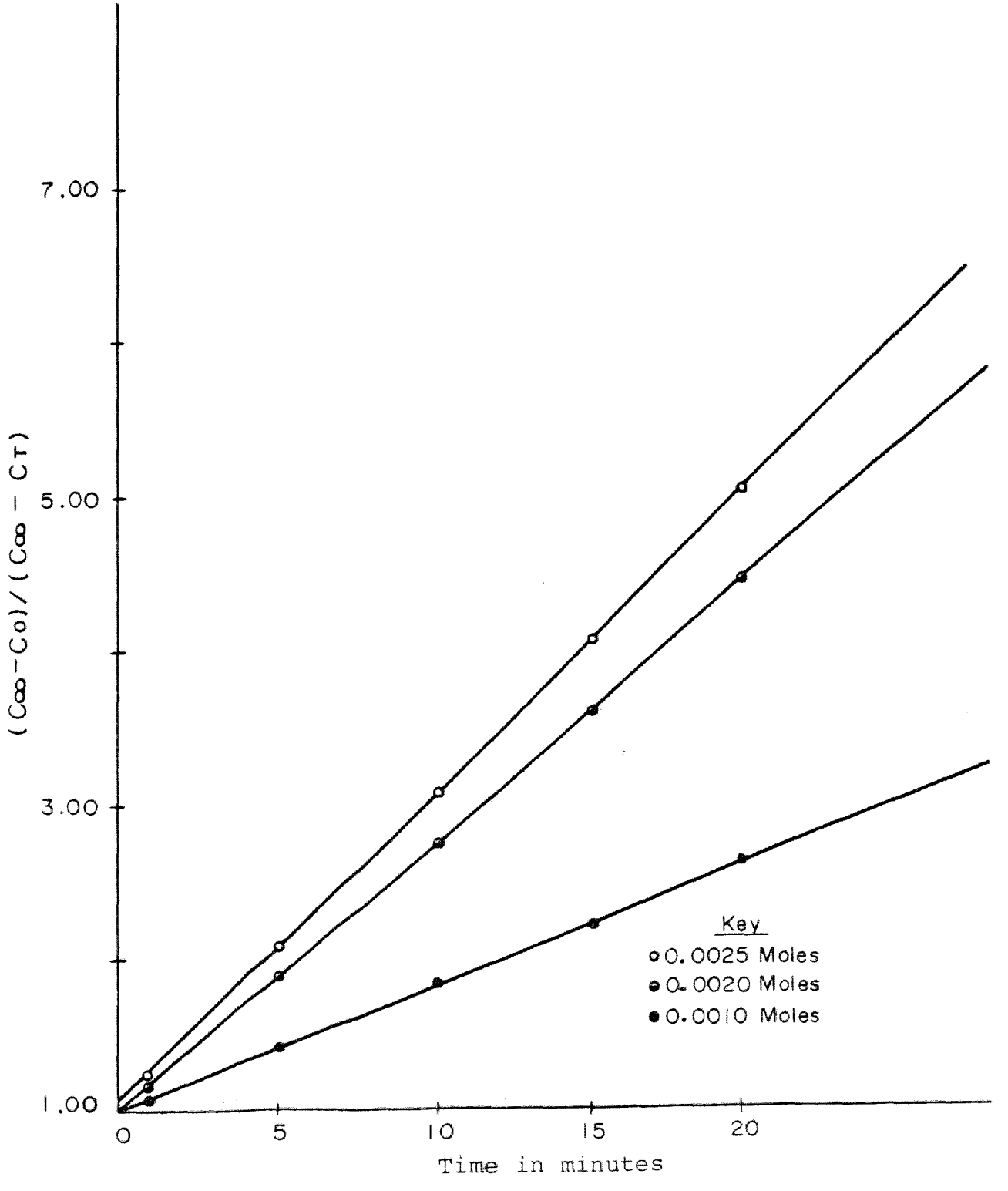



Figure 9. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with ETOH in cell 1 at 25.0°C.

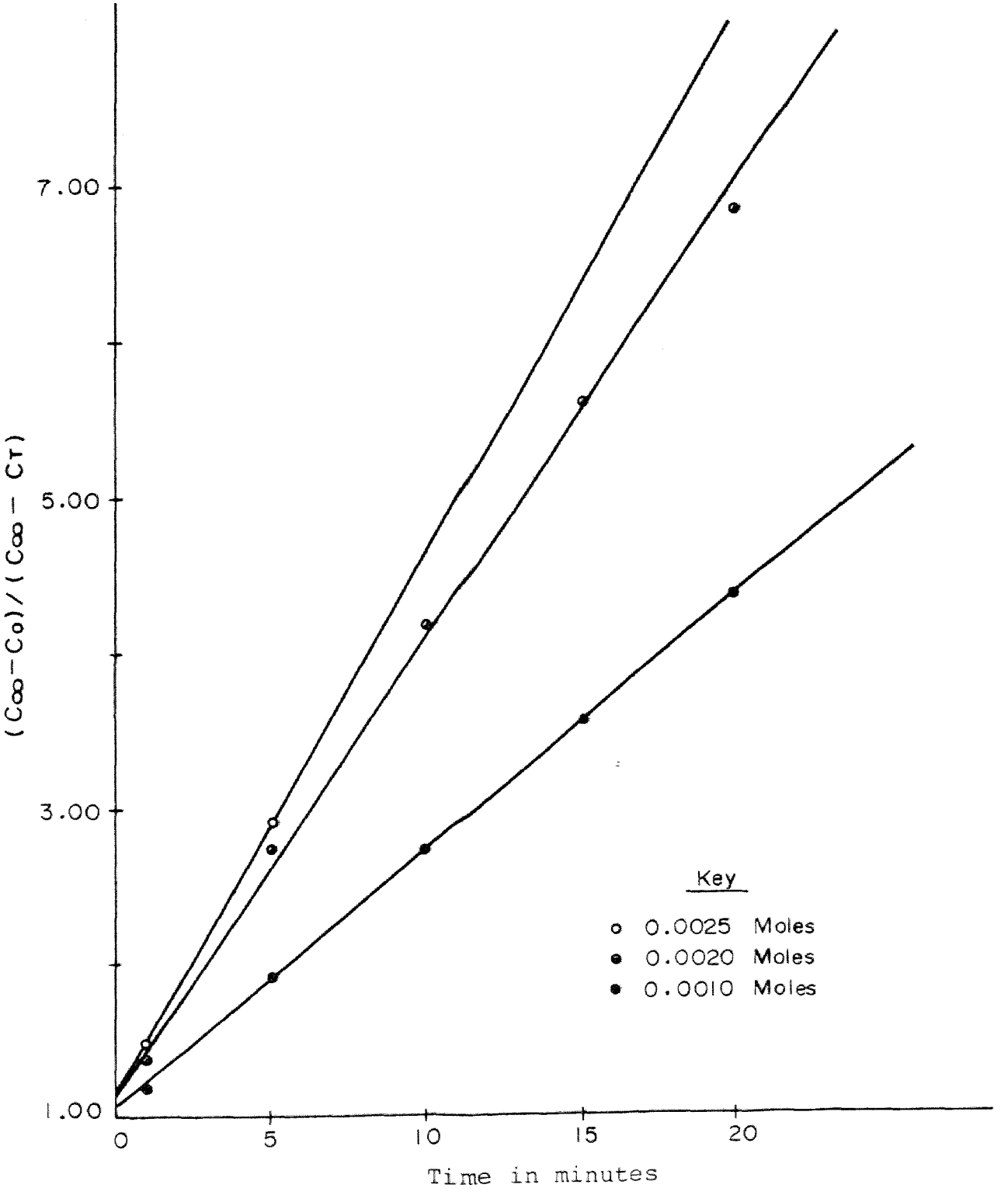



Figure 10. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with ETOH in cell 2 at 25.0°C.

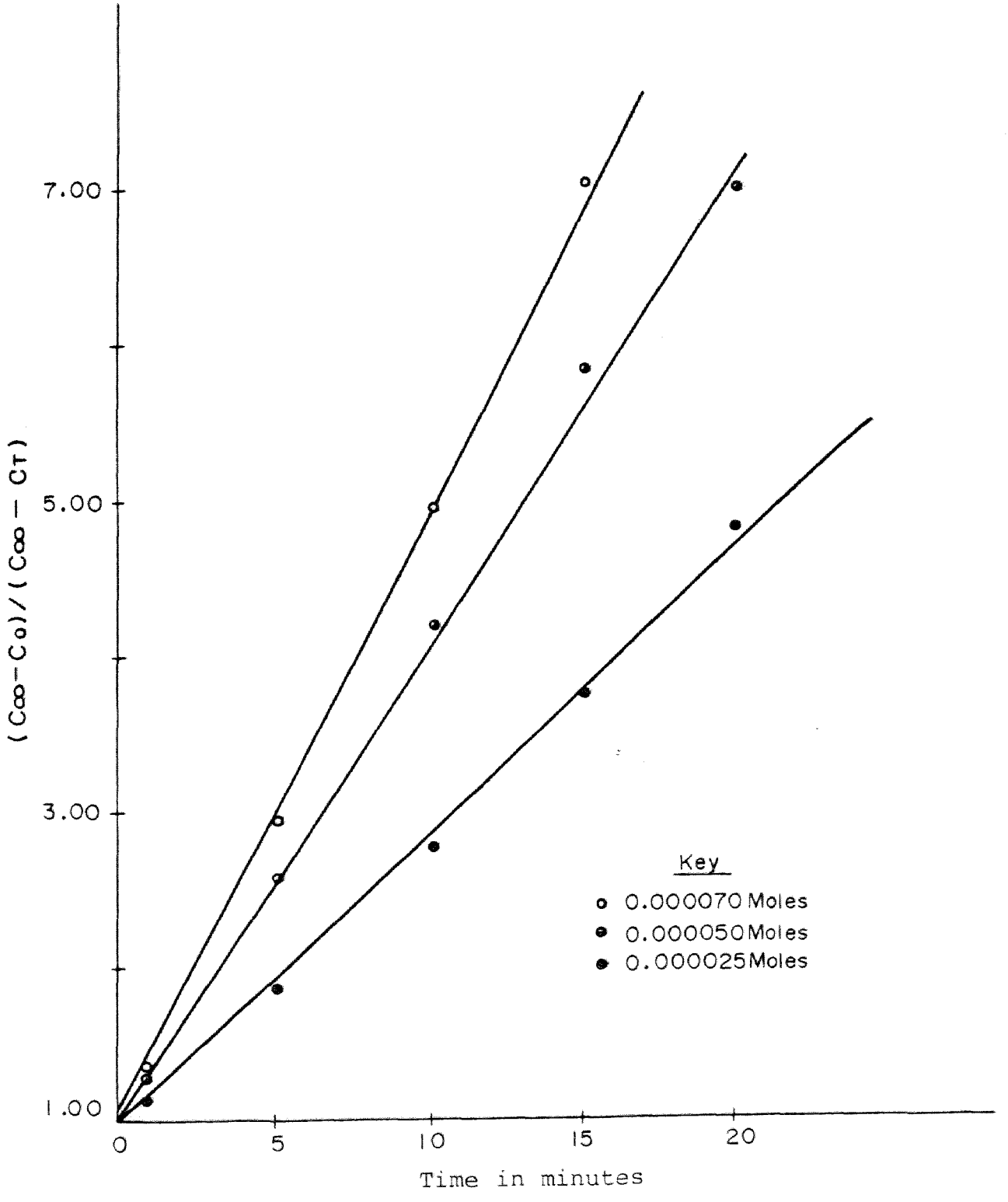



Figure 11. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 1 at 25.0°C.

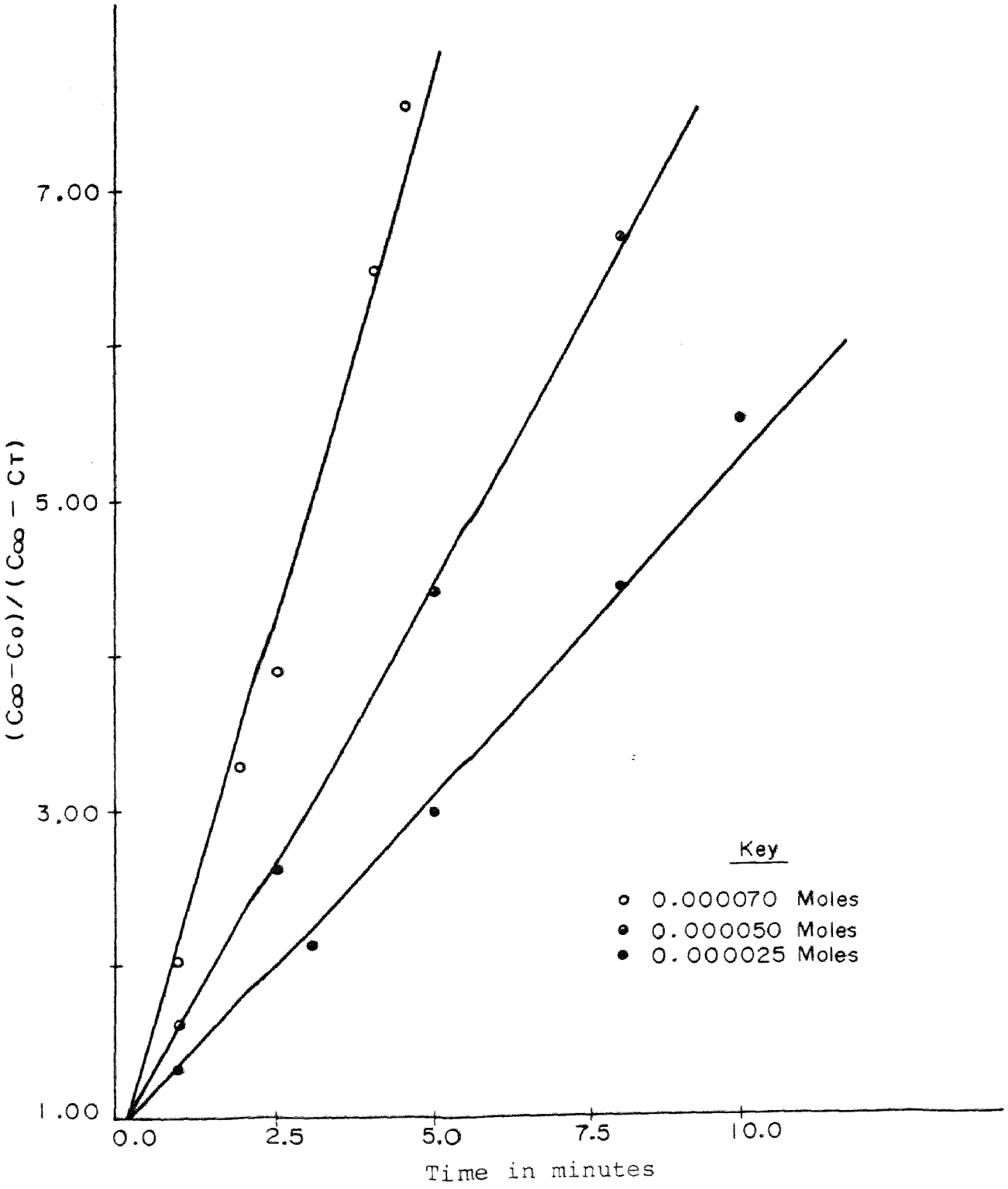



Figure 12. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 2 at 25.0°C.

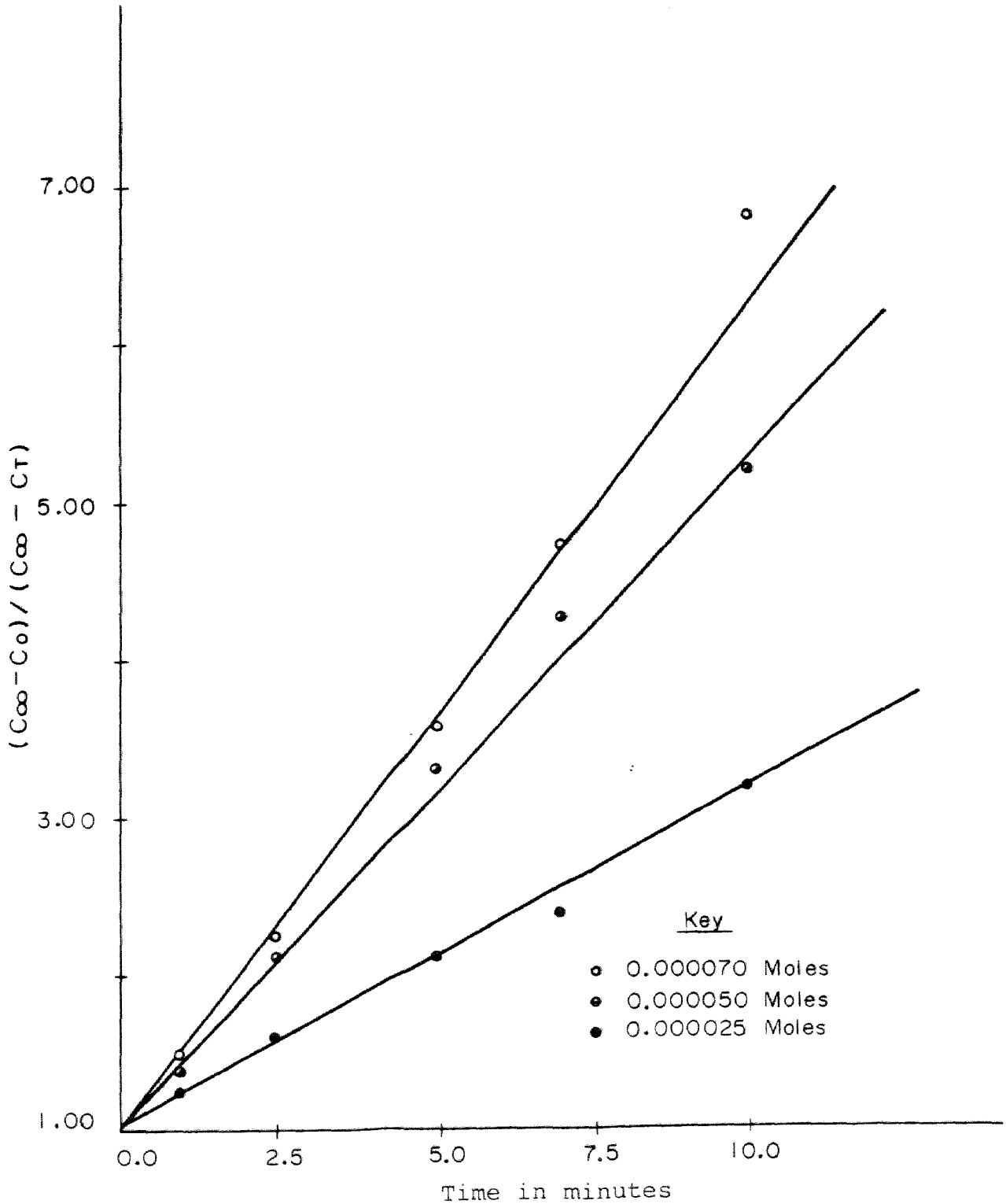



Figure 13. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 1 at 35.0°C.

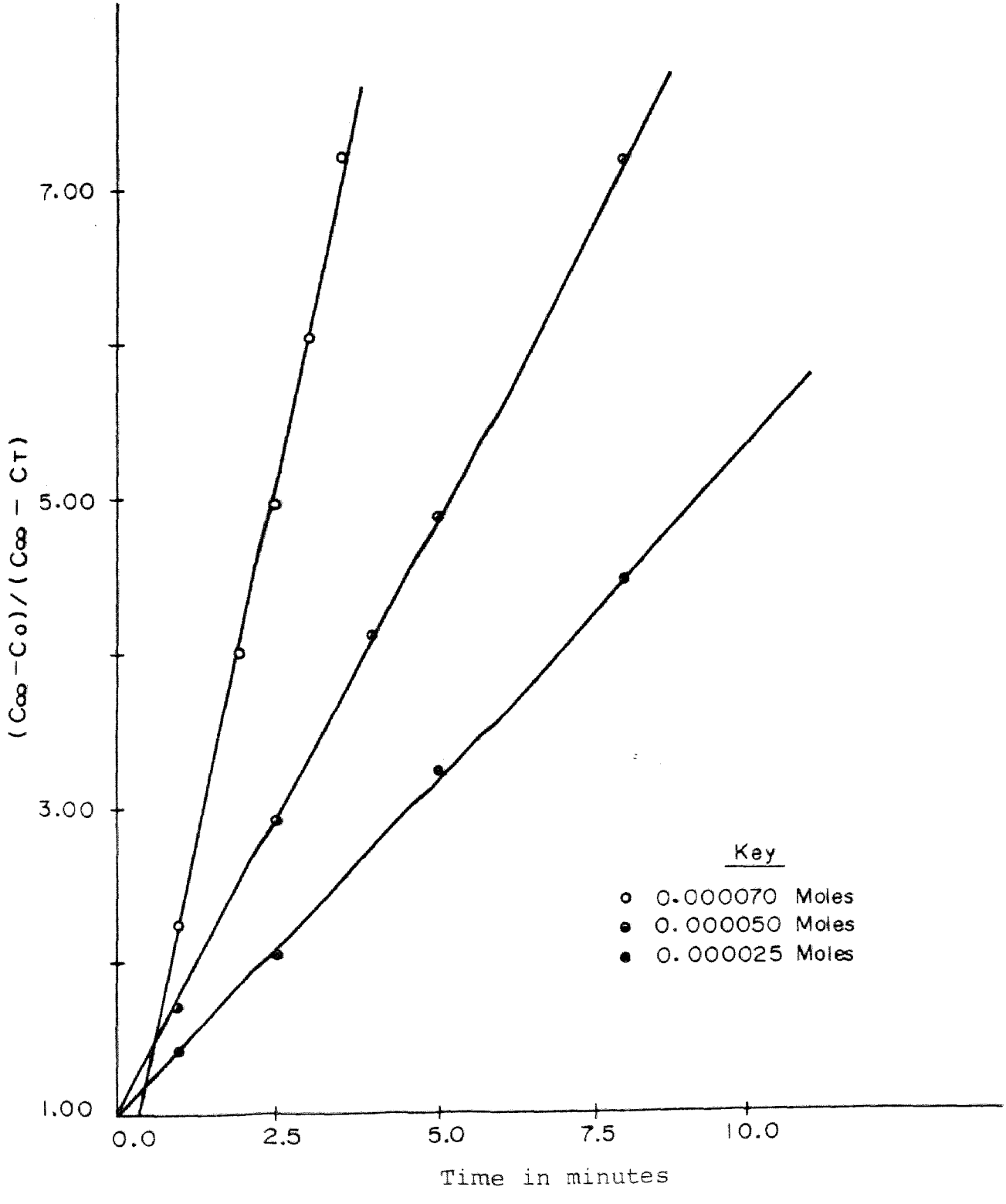



Figure 14. Increase in conductance ratio with time: 2,4-dinitrochlorobenzene with DMSO in cell 2 at 35.0°C.

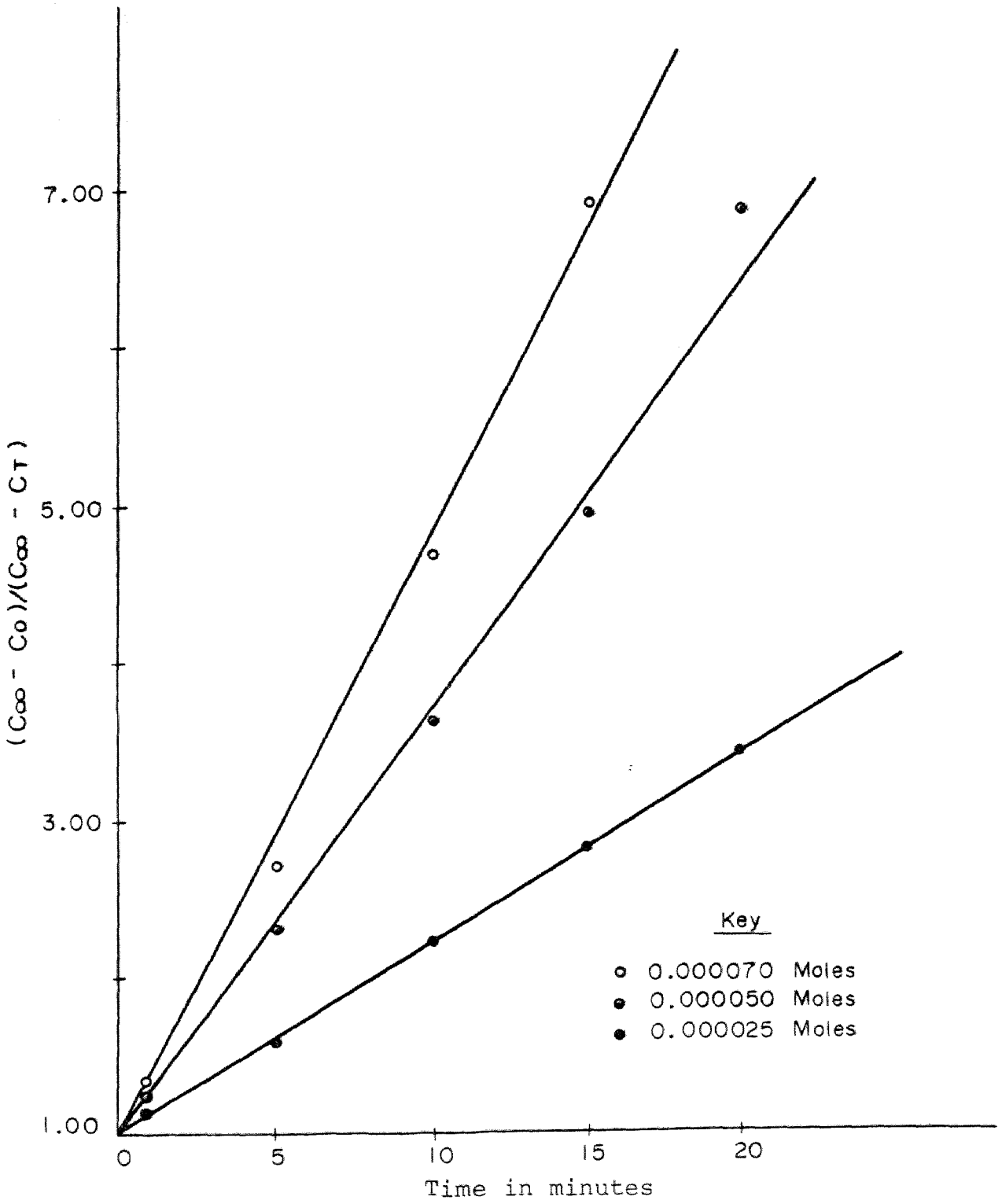



Figure 15. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 1 at 25.0°C.

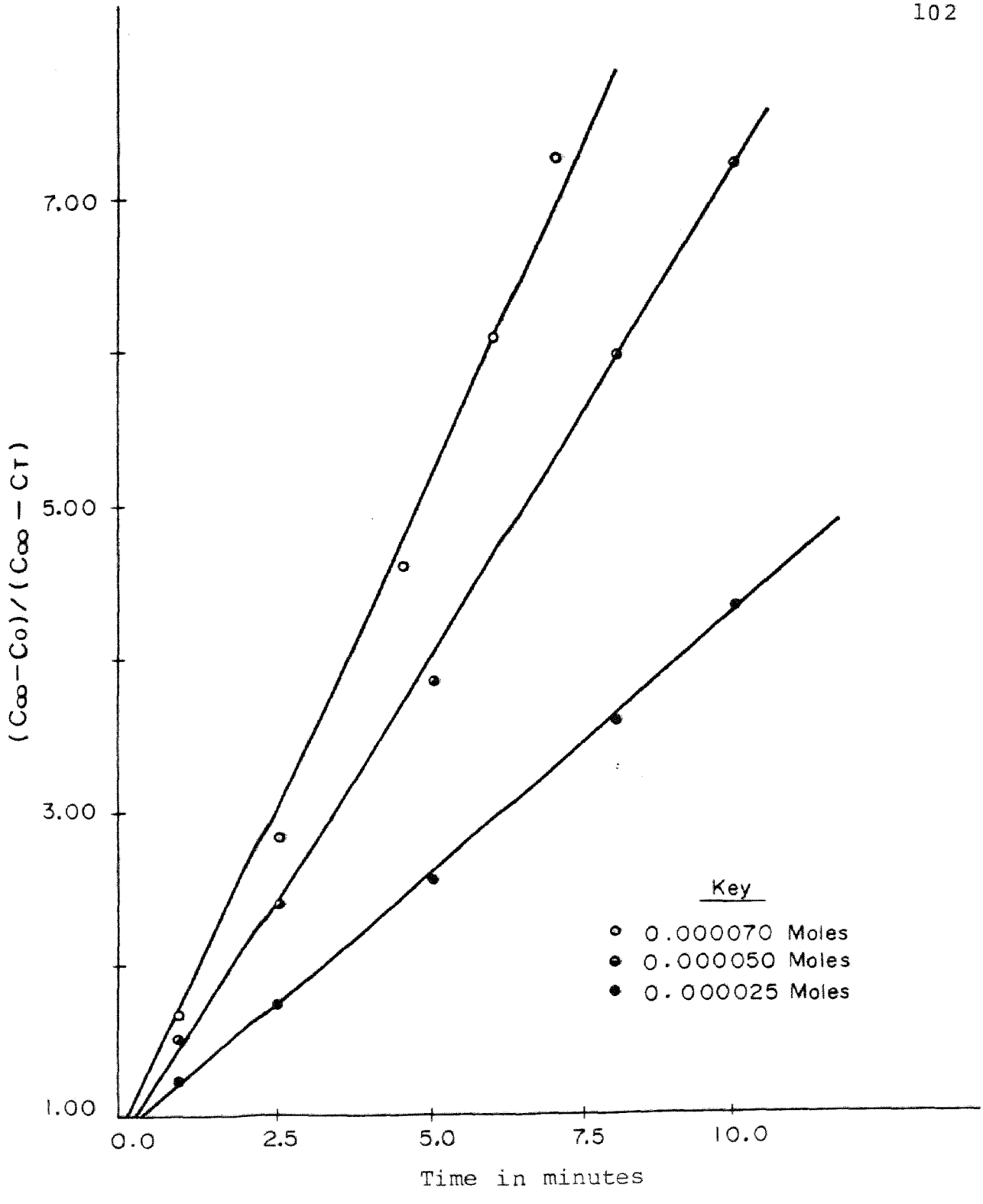



Figure 16. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 2 at 25.0°C.

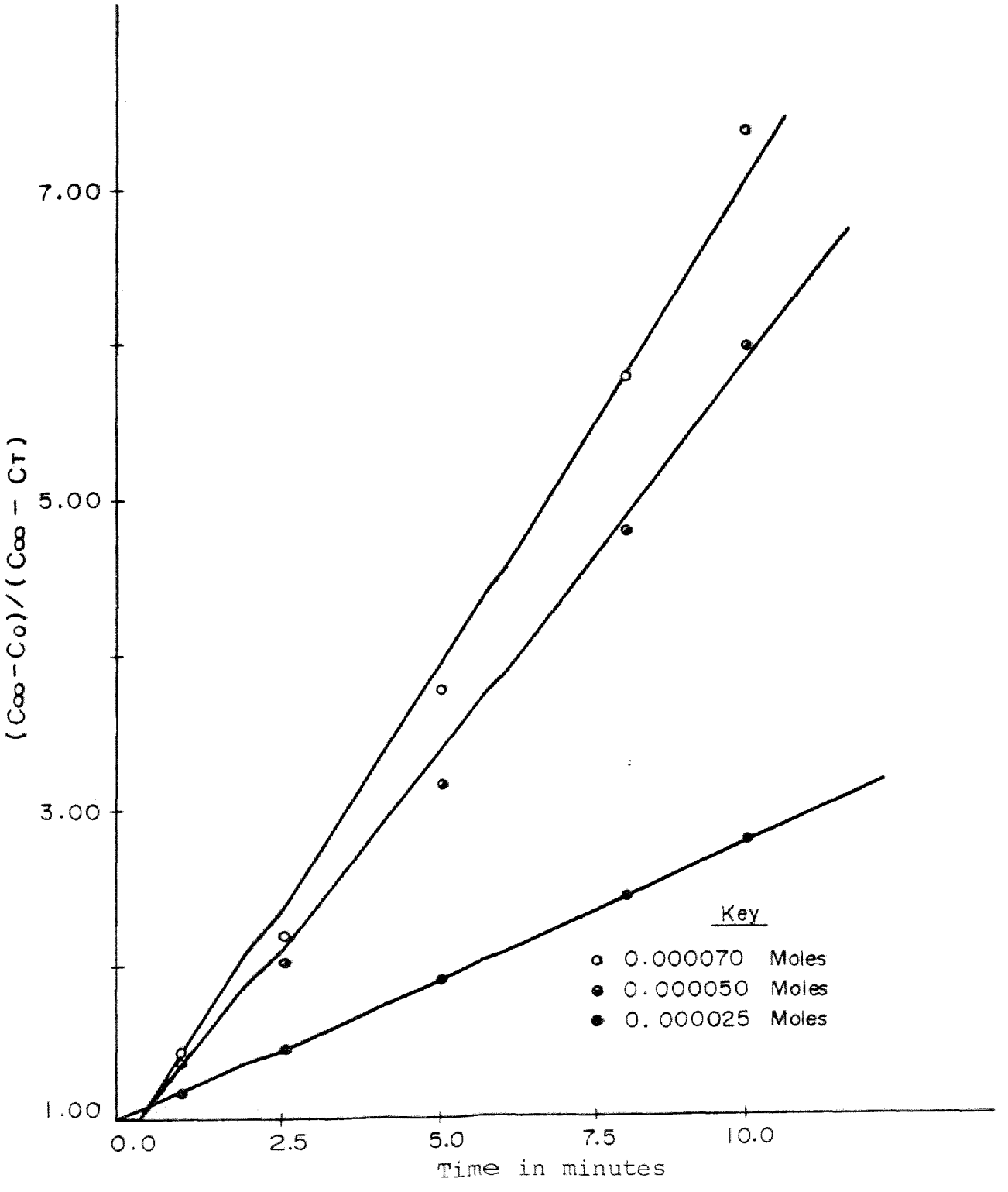



Figure 17. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 1 at 35.0°C.

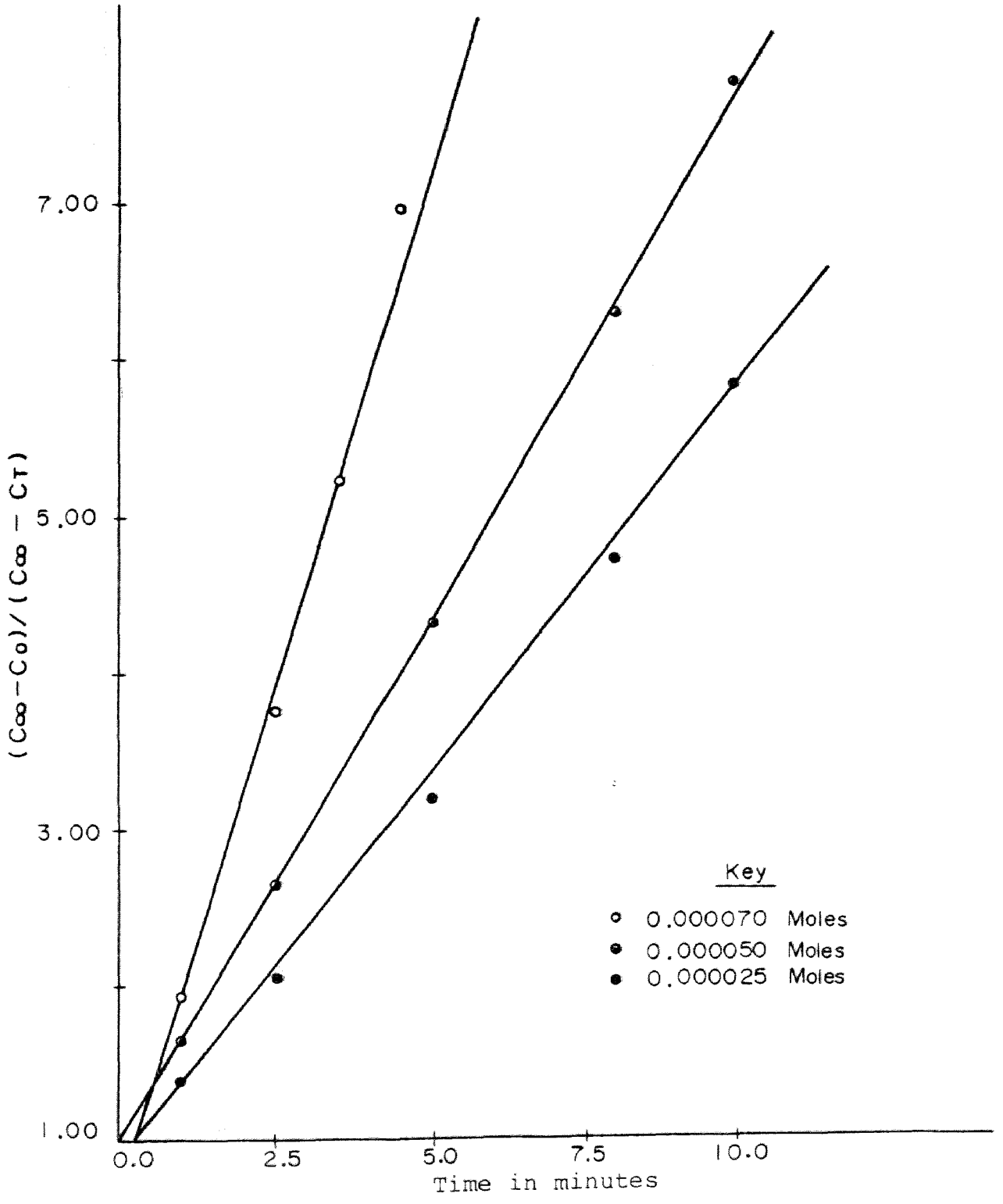



Figure 18. Increase in conductance ratio with time: 2,4-dinitrobromobenzene with DMSO in cell 2 at 35.0°C.

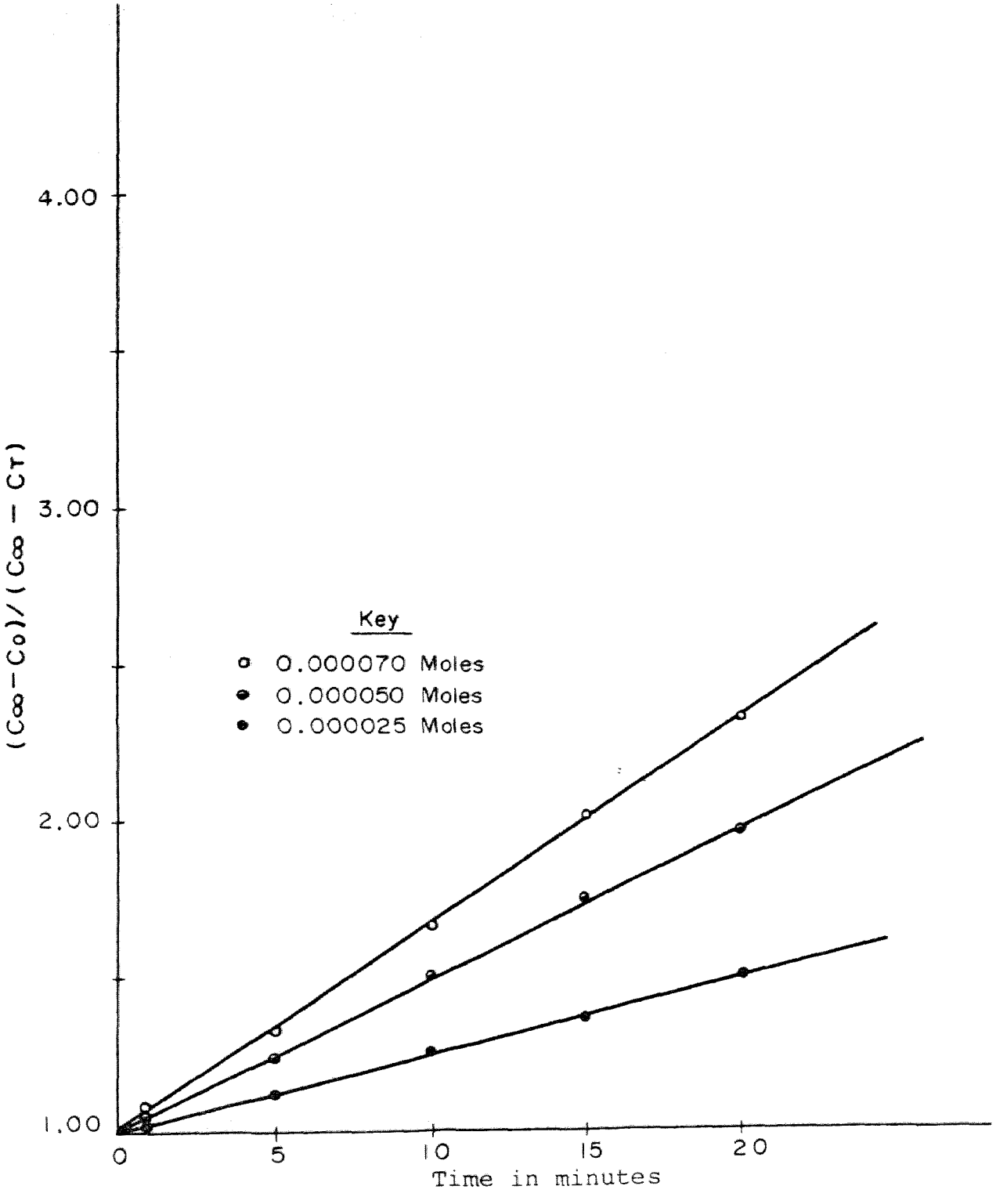



Figure 19. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 1 at 25.0°C.

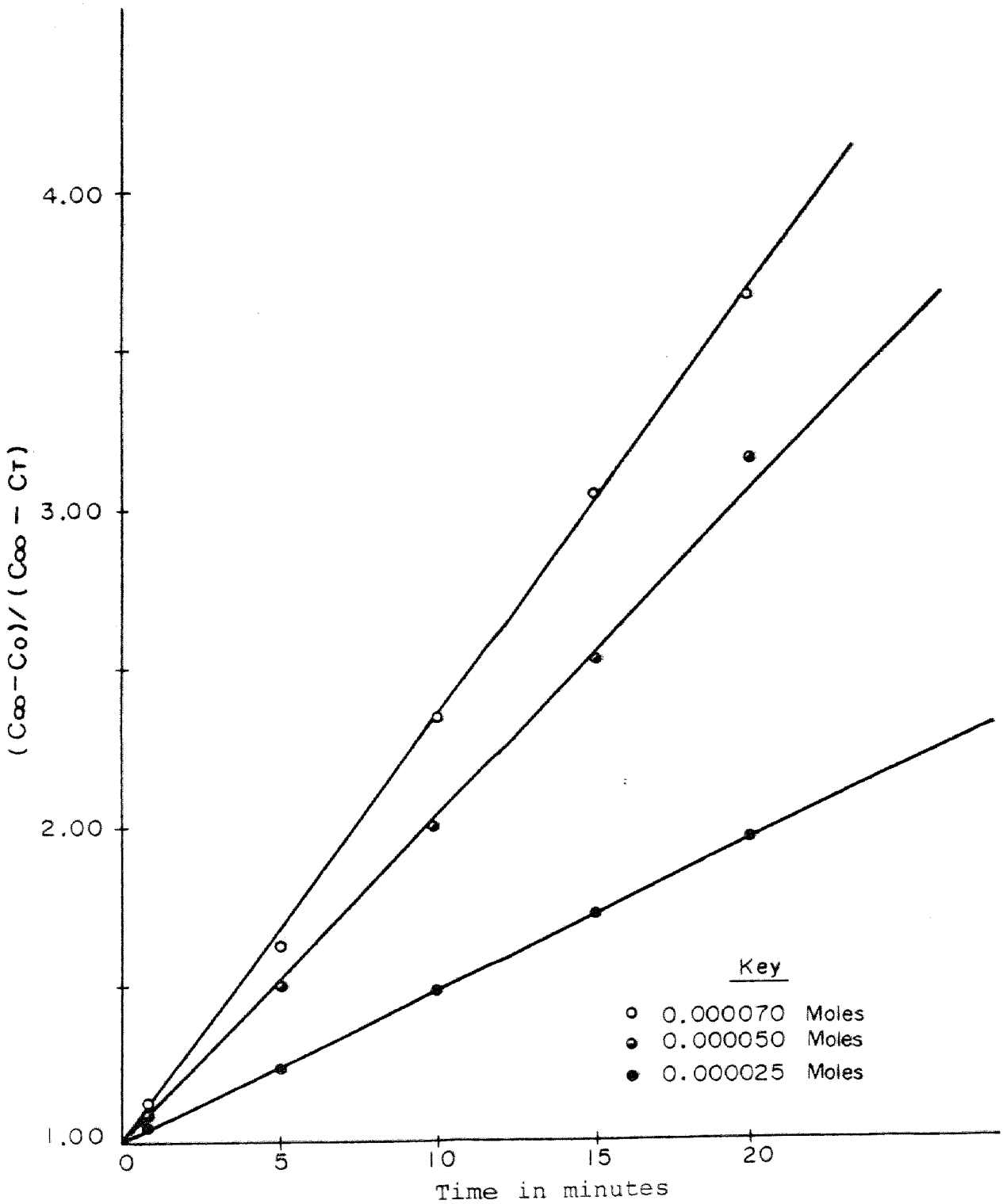



Figure 20. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 2 at 25.0°C.

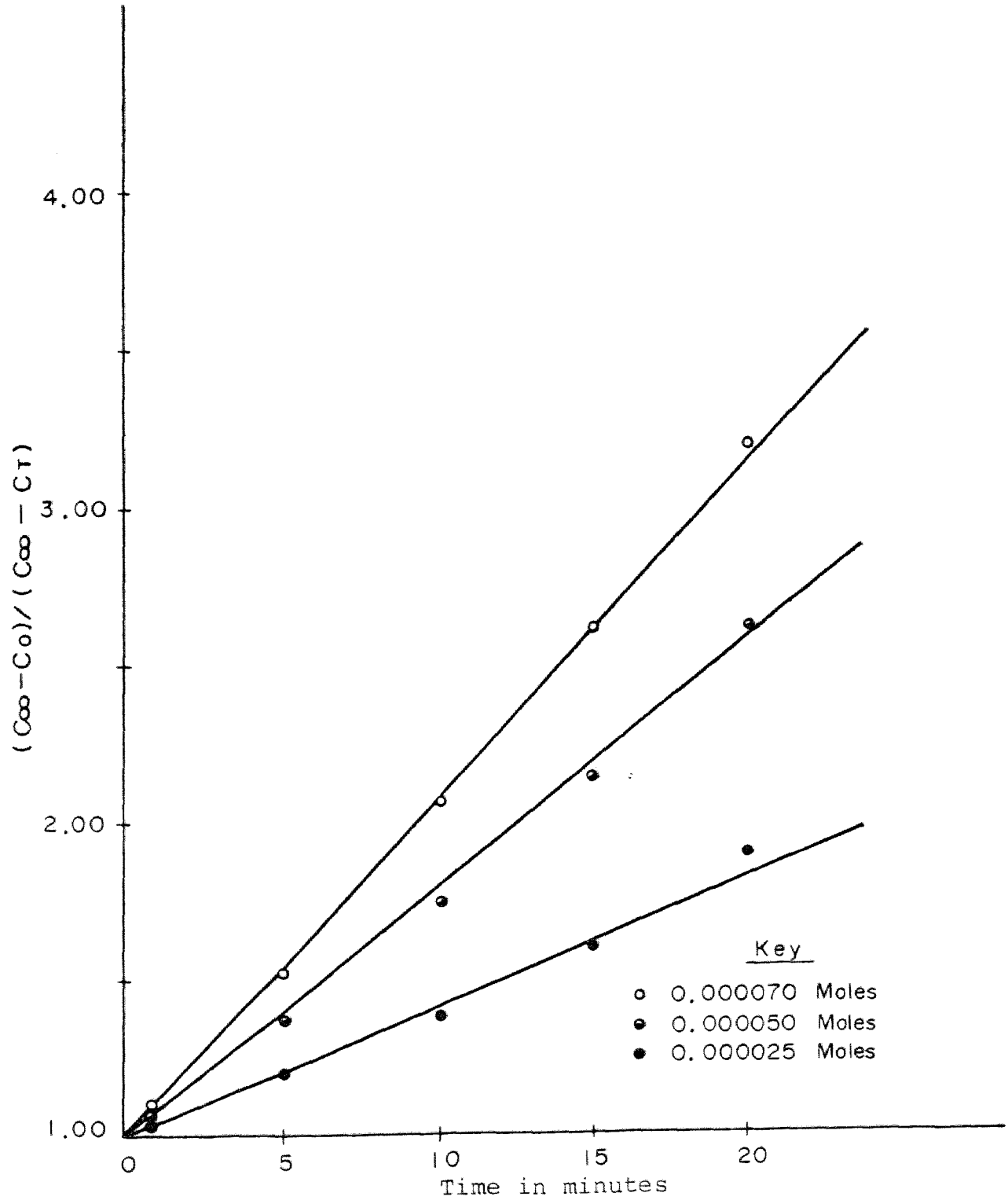



Figure 21. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 1 at 35.0°C.

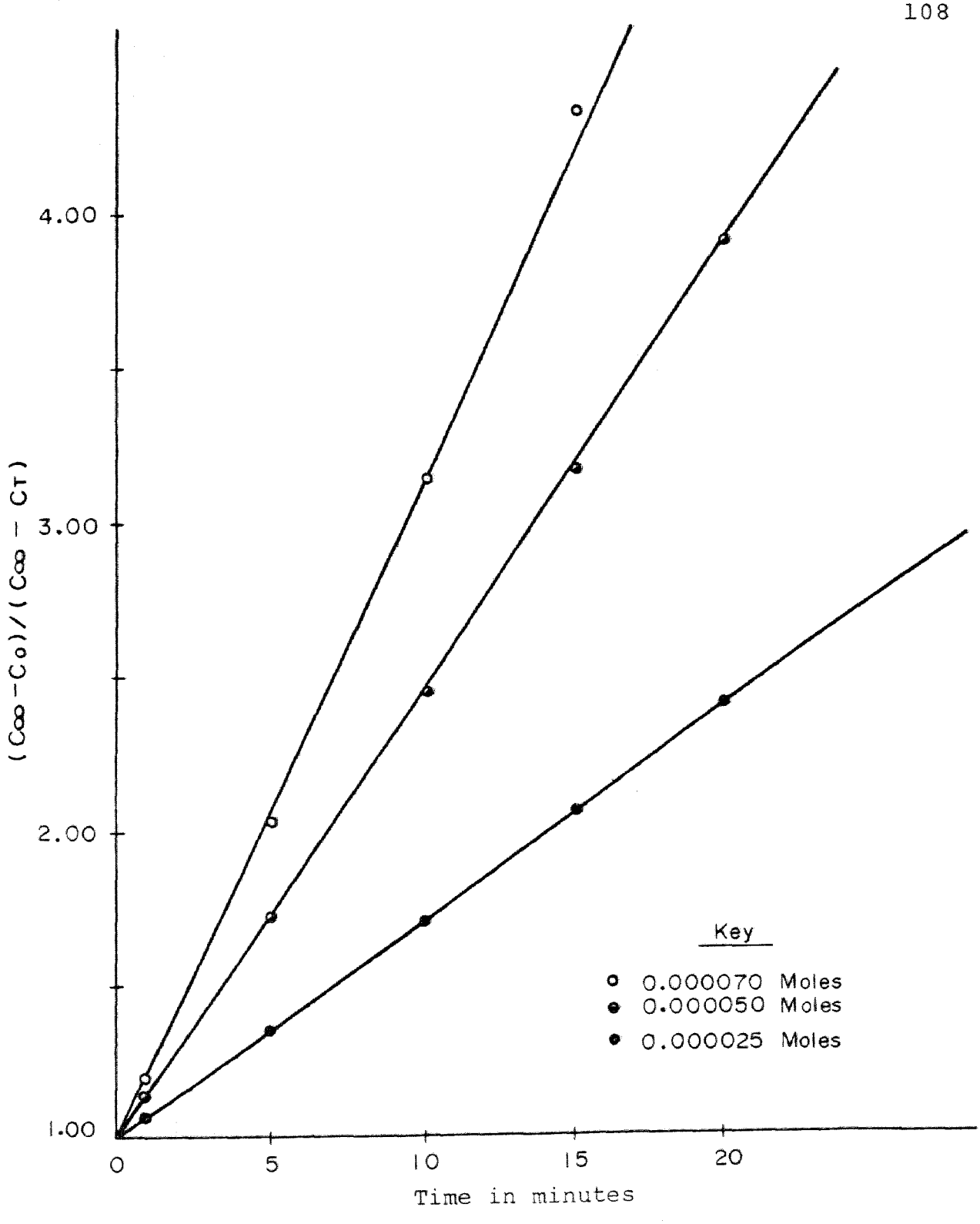



Figure 22. Increase in conductance ratio with time: 2,4-dinitroiodobenzene with DMSO in cell 2 at 35.0°C.

# CHAPTER IV

## CONCLUSIONS AND DISCUSSION

Determination of cell constants. Table XLIV shows the reproducibility of cells 1 and 2, as determined from their cell constants before and after the rate studies. The accuracy of conductance measurements was limited to four significant figures.

TABLE XLIV

REPRODUCIBILITY OF CELL 1 AND CELL 2 AT VARIOUS CONCENTRATIONS OF KCL AT 25.0°C

| | Cell 1 | | Cell 2 | |
|---|---|---|---|---|
| KCl, M | Cell Constant in $cm^{-1}$ | Resistance of cell in ohms | Cell Constant in $cm^{-1}$ | Resistance of cell in ohms |
| 0.00100 | 1.4113±.0025 | 9607 | .1544±.0002 | 1051 |
| 0.00500 | 1.4165±.0018 | 1974 | .1555±.0005 | 216.7 |
| 0.01000 | 1.4247±.0056 | 1008 | .1566±.0002 | 110.8 |

The change in cell constant was also observed by Frank and by Berkland, who prepared new solutions, but obtained the same results. In this study an upward drift in conductance between several determinations of solution conductance at a specific concentration was observed, but

attributed to poor grounding or temperature drift since the change was small. Youngberg (49) observed that the conductance of the solution tended to increase while it was being measured, but stopped when the solution was removed from the cell. A similar phenomena was noted by Noyes (95) when measuring HCl solutions. Youngberg indicates this is probably caused by ions, which were absorbed during platinization, going into solution from the platinum black surface, since the problem was overcome by allowing the cells to stand filled with conductivity water for several weeks.

The deviations, while being consistent for both cells, are higher for cell 1 than cell 2. However, the relative deviations for both cells are approximately the same. Cell 2 was replatinized during the preliminary studies in ethanol. The measurements of the cell constants after the reaction rate study in DMSO were higher for cell 1 and lower for cell 2. This same trend was observed by Berkland and attributed to experimental error in the measurement since the deviations were small. The cell constant variance represents an overall effect, since, other than for the replatinization of cell 2, the cell constant was not determined between runs. Following the initial determination of the cell constants and establishment of the relative precision of a conductance measurement, the reaction in ethanol was performed to gain facility with the

equipment and check the reproducibility of the work by Frank and by Berkland.

The 2,4-dinitrochlorobenzene reaction in ethanol (ETOH). This reaction was run to check the measuring system and relate this study to those of C. O. Frank and T. R. Berkland. The data obtained for the reaction at 25.0°C is listed in Tables II through VII and in Figures 9 and 10. The recorded times were plotted against the conductivity ratios and the parameters were calculated using a least squares technique. Table XLV contains the slopes of the lines, y-intercepts, and coefficients of determination. The rate constants, half-lives, and reaction order with respect to time are recorded in Table XLVI.

A reasonable fit of the data to equation (33), which was developed for a second order reaction, is indicated by the calculated y-intercepts and the coefficients of determination which are both close to their respective theoretical values of 1.00. Furthermore, the reaction order with respect to time ($n_t$) is close to the theoretical value of 2.00 lending further credence to equation (33).

Youngberg determined the initial conductance $C_o$ by extrapolating to time zero the conductance values for the first few minutes of the reaction, since the measurement of the piperidine solution conductance, the major contributor, varied by as much as 100%. In this study a similar technique was employed for the determination of the initial

TABLE XLV

SLOPES, Y-INTERCEPTS, AND COEFFICIENTS OF DETERMINATION FOR THE 2,4-DINITROCHLOROBENZENE REACTION AT 25.0°C IN ETOH

| Moles of DNCB/ 40.0 ml cell volume | Slope | Y-intercept | Coefficient of determination |
|---|---|---|---|
| | | Cell 1 | |
| .00100 | .0844 | .985 | .9996 |
| .00200 | .1770 | .999 | .9999 |
| .00250 | .2034 | 1.035 | .9998 |
| Moles of DNCB/ 20.0 ml cell volume | | Cell 2 | |
| .00100 | .1738 | 1.010 | .9994 |
| .00200 | .3212 | 1.066 | .9970 |
| .00250 | .3985 | 1.021 | .9964 |

TABLE XLVI

RATE CONSTANT, HALF-LIFE, AND REACTION ORDER FOR THE 2,4-DINITROCHLOROBENZENE REACTION AT 25.0°C IN ETOH

| Moles of DNCB/ 40.0 ml cell volume | rate k ($l\ mol^{-1}\ min^{-1}$) | $t_{\frac{1}{2}}$ (minutes) | $n_t$ |
|---|---|---|---|
| | Cell 1 | | |
| .00100 | 1.688 | 11.85 | 2.03 |
| .00200 | 1.770 | 5.65 | 2.05 |
| .00250 | 1.627 | 4.92 | 2.13 |
| Moles of DNCB/ 20.0 ml cell volume | Cell 2 | | |
| .00100 | 1.738 | 5.75 | 2.10 |
| .00200 | 1.606 | 3.11 | 2.17 |
| .00250 | 1.594 | 2.51 | 2.11 |

conductances of the DMSO reactions, with the only difference being that the log of the conductance was plotted against time and extrapolated to time zero. This was more convenient because the conductance increased very rapidly making scaling difficult. As noted by Youngberg this problem was not discussed by either Berkland or Frank. The initial conductance values determined by Berkland for the bromo and iodo reactions in ethanol appear internally consistent on the basis of the ratios of the initial conductance ($C_o$) at different concentrations as compared with the infinity conductance ratios for the same concentrations. Frank's initial conductance values for the chloro reaction at 25.0°C, however, had some discrepancies and do not permit a comparison with Berkland's initial conductance values for the same reaction. Similar difficulties with the initial conductance values in this study made it necessary to determine by extrapolation the initial conductance values for the chloro reaction in ethanol at 25.0°C for all three studies. The extrapolated and measured values of the initial conductances are listed in Table XLVII. The extrapolated $C_o$ values were used in calculating the conductance ratios of all three studies. In addition to this, some errors were found in the calculations of Frank and Berkland. Before a comparison of all three studies could be made it was necessary to recalculate their data for the chloro reaction.

TABLE XLVII

EXTRAPOLATED AND MEASURED $C_0$ VALUES FOR FRANK, BERKLAND AND THIS STUDY FOR 2,4-DINITROCHLOROBENZENE AT 25°C IN ETOH

| | Moles of DNCB/ cell volume | Extrapolated Cell | | Measured Cell | |
|---|---|---|---|---|---|
| | | 1 | 2 | 1 | 2 |
| | .00100 | 10.59[a] | 195.2 | 5.20 | 61.00 |
| Frank | .00200 | 20.50 | 446.7 | 5.00 | 76.00 |
| | .00250 | 32.70 | 566.0 | 5.90 | 85.00 |
| | .00100 | 10.36 | 195.3 | 5.95 | 64.90 |
| Berkland | .00200 | 20.69 | 358.5 | 8.20 | 122.0 |
| | .00250 | 27.95 | 440.1 | 7.32 | 89.50 |
| | .00100 | 10.10 | 173.8 | 4.70 | 66.02 |
| This study | .00200 | 21.87 | 354.8 | 5.31 | 71.17 |
| | .00250 | 30.44 | 501.2 | 10.50 | 74.50 |

[a]unit: micromhos

The computer program used in this study was used to recalculate the data of both workers for the chloro reaction at 25.0°C and Berkland's data for the 2,4-dinitroiodo and bromobenzene reaction at 25.0° and 40.0°C. Berkland's original notebook was available for this purpose. Unfortunately Frank's was not available and recalculation of his data was accomplished by using for the computer input the reciprocal of the average resistance (average conductance)

for each time interval as two measurements in order that the program function properly. The normal computer printout was obtained except, of course, that the standard deviation and 95% confidence interval for each measurement were zero.

Frank reported an average rate constant of 1.744± .080 l $mol^{-1}$ $min^{-1}$ and Berkland calculated the rate as 1.686±.084 l $mol^{-1}$ $min^{-1}$. In contrast, the recalculated rates for Frank and Berkland are 1.753±.113 and 1.649±.096 respectively as compared with 1.670±.073 l $mol^{-1}$ $min^{-1}$ for this study. The recalculations were checked both by hand and with an electronic calculator. Good agreement was found between some of the original conductance values and the recalculated values.

The rates were recalculated using the extrapolated initial conductances. However, prior to this, the reported rates were recalculated on the basis of the measured conductances. The rates for Frank, Berkland and this study, in this case, were 1.792±.113, 1.699±.094, and 1.746±.078 l $mol^{-1}$ $min^{-1}$ respectively. Actually the rates calculated by Frank and Berkland displayed a double problem, simple calculation error and discrepancies in the initial conductance values. The actual difference in the range between these two sets of recalculated rates is very small and the difference between the average of each set is only 3.2%. This indicates that the initial conductance does not

affect the conductance ratio in proportion to the change in the value of the initial conductance when the extrapolated initial conductance is used.

One possible source of error for both Frank and Berkland is the fact that they performed all calculations for this reaction by hand without the aid of an electronic calculator, though Berkland used a computer in the latter part of his study to determine the slope and intercept by plotting time against the conductance ratio. The recalculated rates for Frank and Berkland and the rates determined in this study are listed in Table XLVIII.

TABLE XLVIII

RECALCULATED REACTION RATES FOR FRANK, BERKLAND AND THIS STUDY FOR THE 2,4-DINITROCHLOROBENZENE REACTION AT 25.0°C IN ETOH

| | Moles of DNCB/cell volume | | | | | |
|---|---|---|---|---|---|---|
| | Cell 1 | | | Cell 2 | | |
| | .001 | .002 | .0025 | .001 | .002 | .0025 |
| Frank | 1.646[a] | 1.895 | 1.816 | 1.597 | 1.750 | 1.813 |
| Berkland | 1.524 | 1.662 | 1.661 | 1.534 | 1.732 | 1.764 |
| This study | 1.688 | 1.770 | 1.627 | 1.738 | 1.606 | 1.594 |

[a]unit: $1\ mol^{-1}\ min^{-1}$

Berkland concluded from a comparison of his rate determination with that of Frank that the measurement of conductance and resistance were at least comparable. It can be seen in Tables II through VII that while variance is rather random with an increase in conductance, the variance of a conductance tended to increase with an increase in conductance. A similar trend was observed by Berkland which is opposite to that obtained by measuring resistance, but the error in ppt was essentially the same for all three studies under discussion; the precision of the measurement becomes greater as the reaction slows down.

The average relative percent deviation of a measurement in Cell 1 in terms of variance was 0.48%, while for Cell 2 it was 1.02%. For Cell 1 used by Berkland the average percent relative deviation was 0.45% and for Cell 2 0.49%. The relative error expressed in terms of the 95% confidence interval was, of course, approximately twice that of the variance. The error in measurements made by Berkland was less than that of this study, but they are both within the equipment's range of reproducibility.

A comparison is made in Table XLIX between the infinity conductances at different concentrations for the three studies. There is good agreement in the infinity ratios between Berkland and this study. The closer ratios in these two studies over the ratios obtained by Frank indicate the infinity conductance measurements ($C_\infty$) were

made closer to the equilibrium point of the reaction by Berkland and this study.

TABLE XLIX

RATIOS OF THE INFINITY CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROCHLOROBENZENE AT 25.0°C IN ETOH

| Moles of DNCB/cell volume | This Study | | Berkland | | Frank | |
|---|---|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | | | $C_\infty/C_\infty$ | | | |
| .0025/.0020 | 1.17 | 1.25 | 1.19 | 1.17 | 1.13 | 1.20 |
| .0020/.0010 | 1.72 | 1.71 | 1.70 | 1.70 | 1.73 | 1.64 |
| .0025/.0010 | 2.05 | 2.14 | 2.02 | 2.03 | 1.97 | 1.98 |

Berkland was unable to compare individual conductances with values obtained by Frank because different concentrations were used in those two studies. For Cell 1 in this study and that of Berkland the same concentrations were used, making possible a comparison of individual conductance values. The conductance values at the three concentrations, 0.0010, .0020, and .0025, of this study were plotted against the corresponding values of Berkland to determine the degree of correlation. The slopes were .9361, .9319, and .9421, respectively, while the coefficients of determination were .9998, .9996, and .9996, respectively. The high degree of correlation indicates a consistency in the measurement technique of the two experimenters. The

slope, while consistent, indicates the concentrations in this study were higher than those used by Berkland.

While inconsistencies in the measured initial conductances do not permit a comparison as done for the infinity conductances, it is possible to calculate the ratios of the extrapolated conductances. These ratios are listed in Table L. The ratios for this study are more consistent than for those of Frank or Berkland. The inconsistencies may in part be due to errors in graphical analysis, measurement errors in making up the piperidine solutions, or in manipulating the syringe used to introduce the piperidine into the reaction cell. The ratios for the infinity conductances in Table XLIX are both closer and lower than for the extrapolated initial conductances. The ratio of (.0025/.0010) displays the greatest difference and also the term (.0025/.0020) is higher than the infinity conductance ratio with the same concentration terms.

Cell 2 of this study exhibited some variation both from Cell 1 of this study and the conductance values for Cell 2 at the .0025 mol concentration level determined by Berkland. The .0025 mol reaction in Cell 2 exceeded the maximum conductance of the bridge (11,111.11 micro mhos) after the reaction had proceeded for 15 minutes. The conductance ratio was plotted against time through the 5 minute point to determine the reaction rate. As noted in the experimental section, crystals of the product,

2,4-dinitrophenylpiperidine were observed forming in Cell 2 on the platinum electrodes after a period of one hour. It appears that the smaller cell volume of Cell 2 in this study (20.0 ml), as compared to the 28.0 ml used by Berkland and the 29.5 ml cell used by Frank, resulted in the formation of a super saturated solution of 2,4-dinitrophenylpiperidine in ethanol during the course of the reaction. The formation of crystals on the platinum electrodes would alter the surface area of the electrodes, thereby changing the value of the measured conductance from the true value, accounting in part for the problems encountered with Cell 2 at 0.0025 moles concentration.

TABLE L

RATIOS OF THE INITIAL CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROCHLOROBENZENE AT 25.0°C IN ETOH

| Moles of DNCB/cell volume | This Study | | Berkland | | Frank | |
|---|---|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | | | $C_o/C_o$ | | | |
| .0025/.0020 | 1.39 | 1.41 | 1.35 | 1.23 | 1.59 | 1.27 |
| .0020/.0010 | 2.16 | 2.04 | 2.00 | 1.83 | 1.93 | 2.29 |
| .0025/.0010 | 3.01 | 2.88 | 2.70 | 2.25 | 3.09 | 2.89 |

Since three independent experimenters have determined the rate constant under essentially the same conditions, an analysis of variance (96) can be performed on the rate constants with respect to cell, concentration, and

experimenter. Table XLVIII was the design model for the variance analysis where experimenters (method) and concentrations are considered fixed variables and Cell 1 and Cell 2 are considered random variables. The source of variation, degrees of freedom, and the analysis of variance terms SS, sum of the squares, MS, mean square, and F test ratio are listed in Table LI. The calculation formulas for the SS terms and F test ratios are listed in Appendix II.

Looking up the F values in an F test table (96) yields the following conclusions at both the 0.05 and 0.01 probability levels. There is no significant variation attributable to concentration, cell, experimenter, interaction of concentration and experimenter, or the interaction of cell and concentration. On the basis of the ANOVA results it would seem plausible to combine the 18 rate constants in Table XLVIII to obtain a more representative value for the rate of 2,4-dinitrochlorobenzene in ethanol at 25.0°C. The rate then becomes 1.691 l $mol^{-1}$ $min^{-1}$ ± .094.

Since the rate constant determined by this study was in agreement with the corrected values determined by Frank and by Berkland, the halogen series was reacted with piperidine in DMSO at 25.0°C and 35.0°C in order to determine the rate constants, halogen series, and activation energies and entropies.

TABLE LI

ANALYSIS OF VARIANCE OF EXPERIMENTERS, CONCENTRATIONS, AND CELLS FOR THE REACTION OF 2,4-DINITROCHLOROBENZENE WITH PIPERIDINE AT 25.0°C IN ETOH

| Source of Variation | d.f. | SS | MS=SS/d.f. | F |
|---|---|---|---|---|
| Concentration | 2 | .041631 | .020816 | .4988 |
| Cell | 1 | .002568 | .002568 | .060122 |
| Experimenter | 2 | .035958 | .017979 | 2.987 |
| Concentration X Cell | 2 | .000129 | .000064 | .01278 |
| Concentration X Experimenter | 4 | .058919 | .014730 | 2.943 |
| Cell X Experimenter | 2 | .012038 | .006019 | 1.203 |
| Concentration X Cell X Experimenter (error term) | 4 | .020018 | .005004 | |

d.f. = degrees of freedom; SS = sum of the squares; MS = mean square; F = MS/error MS (calculated F value test ratio), see Appendix II.

Reactions in Dimethylsulfoxide (DMSO). The reactions in DMSO were, as expected, much faster than those in ethanol which necessitated using approximately one-hundredth of the concentrations used for the chloro reactions in ethanol. As noted in the experimental section, DMSO solutions of 2,4-dinitrochlorobenzene displayed a deeper color than the ethanol solutions even though the DMSO solutions were less concentrated. A solution of

2,4-dinitrochlorobenzene in DMSO ($5 \times 10^{-5}$ mol/30 ml) was prepared and the conductance monitored. The conductance changed slowly over several hours to a constant value. The recovered material was shown by melting point to be the original 2,4-dinitrochlorobenzene. Several runs were made with a solution that had been allowed to stand for several days and consistent results were obtained between runs.

Ritchie and Pratt (55) reported that DMSO "may form dimers: as well as weak 1:1 complexes due to antiparallel, electrostatic multipolar interactions involving localized polar groups rather than entire molecules." This might account for the greater color intensity in DMSO and might in part explain the change in conductance observed. Nevertheless, a change in conductance with time would not be expected, but rather an instantaneous increase upon mixing. Color change was not monitored with a spectrophotometer.

As reported by Youngberg (49), ions on the platinum electrodes may go back into solution producing an increase in conductance over time. Given the good solvent properties of DMSO, this might in part account for the change, or drift, in conductance observed. However, a color change is usually indicative of chemical reaction between two species.

Kolthoff and Reddy reported DMSO decomposition when refluxed over CaO or BaO and that removal of decomposition products, which were not identified, was impossible (97). The following scheme (Fig. 23) has been suggested for the

$$(CH_3)_2SO \longrightarrow CH_3SH + HCHO \longrightarrow (HCHO)_X \quad (48)$$

$$2\ CH_3SH + HCHO \longrightarrow (CH_3S)_2CH_2 + H_2O \quad (49)$$

$$2\ CH_3SH + (CH_3)_2SO \longrightarrow CH_3SSCH_3 + CH_3SCH_3 + H_2O \quad (50)$$

$$2\ (CH_3)_2SO \longrightarrow CH_3SO_2CH_3 + CH_3SCH_3 \quad (51)$$

Figure 23. Suggested scheme for decomposition of dimethyl sulfoxide (ref. 98).

generation of decomposition products (98). The compounds dimethyl sulfide, dimethyl disulfide and bis-methylthiomethane could react with 2,4-dinitrohalobenzene. The reaction of dimethylsulfide with 2,4-dinitrohalobenzene (99) yields a compound ($C_{12}H_8N_2O_4S$) of molecular weight 276.28, which when crystallized from benzene yields pale yellow needles, mp 117°C. The amount of such impurities, if present, in the distilled DMSO was very small as evidenced by the small change in conductance. Hence, the relative rates of the various halo-compounds would not be affected.

The Chloro Reaction. The data for the reaction of 2,4-dinitrochlorobenzene with piperidine in DMSO are listed in Tables VIII through XIX and Figures 11 through 14. The slopes, y-intercepts, and coefficients of determination are listed in Table LII. The rate constants, half-lifes, and reaction orders are listed in Table LIII.

The maximum recorded conductances in Cell 1 and Cell 2 were approximately 50 and 800 micromhos respectively. This is much less than the comparable values for the chloro reaction in ethanol of 800 and 12,600 micromhos for Cell 1 and Cell 2, respectively. While lower than the conductances for the ethanol reaction, the same value ranges for the conductance ratio were obtained. The reaction in ethanol required approximately 60 minutes to reach 80% completion, while only 30 minutes was required for the lowest concentration DMSO reaction in Cell 1.

TABLE LII

SLOPES, Y-INTERCEPTS, AND COEFFICIENTS OF DETERMINATION FOR THE 2,4-DINITROCHLOROBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNCB/ 40.0 ml cell volume | Slope | | y-intercept | | CD | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | .1875 | .2383 | .989 | 1.031 | .9997 | .9989 |
| 0.000050 | .3406 | .5632 | 1.002 | 1.045 | .9999 | .9991 |
| 0.000070 | .4350 | .6105 | 1.013 | 1.046 | .9996 | .9995 |
| Moles of DNCB/ 20.0ml cell volume | | | Cell 2 | | | |
| 0.000025 | .3921 | .4625 | .933 | 1.005 | .9998 | .9996 |
| 0.000050 | .7211 | .8935 | .900 | .992 | .9998 | .9998 |
| 0.000070 | 1.041 | 1.507 | .907 | .905 | .9982 | .9906 |

The error of a measurement tended to increase with concentration, temperature and time, but this is misleading since the relative error became less as the reaction slowed down. The average percent relative deviation of a measurement for Cell 1 and Cell 2 at 25.0°C was 1.54 and 0.51% respectively. For the ethanol reaction in this study, Cell 1 had a lower relative percent deviation than Cell 2 with the average for both cells being 0.75%, while for Berkland's data the values are nearly the same for Cell 1 and Cell 2

with an average of 0.47%. The higher error of 1.0% in DMSO can probably be attributed to the faster rate of reaction. Nevertheless, this error is within the reproducible range of the equipment.

TABLE LIII

RATE CONSTANT, HALF-LIFE, AND REACTION ORDER FOR THE 2,4-DINITROCHLOROBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNCB/ 40.0 ml cell volume | rate k ($l\ mol^{-1}\ min^{-1}$) | | $t_{\frac{1}{2}}$ (min) | | $n_t$ | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | 150.0 | 190.6 | 5.33 | 4.20 | 1.85 | 1.96 |
| 0.000050 | 136.0 | 225.0 | 2.93 | 1.78 | 2.18 | 1.86 |
| 0.000070 | 124.1 | 176.5 | 2.21 | 1.64 | 2.02 | 2.18 |
| Moles of DNCB/ 20.0 ml cell volume | | | Cell 2 | | | |
| 0.000025 | 156.8 | 185.0 | 2.55 | 2.16 | 1.85 | 1.86 |
| 0.000050 | 137.3 | 178.7 | 1.45 | 1.12 | 2.01 | 1.82 |
| 0.000070 | 148.7 | 215.2 | .96 | .66 | 1.84 | 1.79 |

For the reaction at 35.0°C the average percent relative deviation of a measurement in cell 1 and cell 2 was approximately the same with an average of 0.47%. The higher error at 25.0°C was probably related to becoming

familiar with the faster reacting system as compared to the ethanol reaction.

The y-intercepts indicate that the relationship of equation (33) is being followed. While several of the values are a little low, being close to 0.900, these are still within the range of values observed for the reaction in ethanol. This lowering of the y-intercept may be due to the fast rate of reaction and the fact that the reaction was plotted through only the first few minutes of the reaction, which have a greater variance than later points. The coefficients of determination indicate a small amount of unexplained error in the measurements. But once again, for the highest concentration in cell 2 at 35.0°C the error appears higher.

The rates listed in Table LIII did not double with a 10°C increase in temperature. Though the range of values for the reaction rate at 25.0°C appears larger than at 35.0°C, actually the standard deviation is approximately the same at both temperatures. The average of the measured rates at 25.0°C and 35.0°C are respectively 142.2 $l\ mol^{-1}\ min^{-1} \pm 11.9$ and 195.2 $l\ mol^{-1}\ min^{-1} \pm 20.00$. The half-lifes show how fast these reactions proceeded as compared to the chloro reactions in ethanol. Hence a smaller number of points were used in the plot of time versus conductance. Running the reaction at a lower temperature, 0°C for example, was impossible because of the 18.5°C

melting point of DMSO. The concentrations used were very dilute and some of the variance in the rate constants may have resulted from filling errors for the cells and the syringe. Using more dilute solutions to realize a slower reaction rate and half-life would probably add to the error since solutions were made by weighing as opposed to volumetric dilution from a stock which would introduce a consistent error into the concentration series.

The reaction order with respect to time should be close to 2.00 if the reaction is, as assumed, second order. The values obtained indicate this is the case.

The infinity conductance ratios are listed in Table LIV. These appear to be very consistent and are in agreement with the ratios calculated for the ethanol reactions.

TABLE LIV

RATIOS OF THE INFINITY CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROCHLOROBENZENE IN DMSO

| Moles of DNCB/ cell volume | 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | $C_\infty/C_\infty$ | | | |
| .000070/.000050 | 1.19 | 1.19 | 1.22 | 1.20 |
| .000050/.000025 | 1.84 | 1.86 | 1.93 | 1.82 |
| .000070/.000025 | 2.20 | 2.22 | 2.35 | 2.18 |

The initial conductances, measured and extrapolated, appear in Table LV. In some cases the agreement between the measured and extrapolated values was good. The extrapolated initial conductance ratios are given in Table LVI. The agreement between values is not as good as for the infinity ratios, but this same type of variance appeared in the initial conductance ratios for the ethanol reaction. This should not be critical since the influence on the conductance ratio is small, with a tendency to shift the intercept without significantly changing the slope.

TABLE LV

EXTRAPOLATED AND MEASURED INITIAL CONDUCTANCES FOR THE 2,4-DINITROCHLOROBENZENE REACTION IN DMSO

| Temperature | Moles of DNCB/ cell volume | Extrapolated | | Measured | |
|---|---|---|---|---|---|
| | | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| 25.0°C | .000025 | 1.53[a] | 25.96 | 1.01 | 22.04 |
| | .000050 | 2.63 | 56.42 | 1.36 | 19.20 |
| | .000070 | 3.63 | 74.13 | .58 | 15.19 |
| 35.0°C | .000025 | 6.02 | 91.10 | 5.30 | 112.70 |
| | .000050 | 12.45 | 161.90 | 9.80 | 129.30 |
| | .000070 | 14.12 | 187.5 | 5.78 | 67.60 |

[a]unit: micromhos

TABLE LVI

RATIOS OF THE INITIAL CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROCHLOROBENZENE IN DMSO

| Moles of DNCB/ cell volume | $C_o/C_o$ 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| .000070/.000050 | 1.38 | 1.31 | 1.13 | 1.16 |
| .000050/.000025 | 1.96 | 2.17 | 2.07 | 1.78 |
| .000070/.000025 | 2.71 | 2.85 | 2.34 | 2.06 |

The conductance changes consistently with respect to the different concentrations as shown by the infinity conductance ratios in Table LVII. The ratio of the infinity conductances at the two temperatures, 25.0°C and 35.0°C, are about the same as the ratio of the rate constants at 35.0°C to 25.0°C for the corresponding concentrations.

TABLE LVII

RATIOS OF INFINITY CONDUCTANCES AT 35.0°C TO 25.0°C FOR THE 2,4-DINITROCHLOROBENZENE REACTION IN DMSO

| Piperidine, M | $C_\infty/C_\infty$ Cell 1 | Cell 2 |
|---|---|---|
| $5.0 \times 10^{-3}$ | 1.25 | 1.30 |
| $1.0 \times 10^{-2}$ | 1.31 | 1.17 |
| $1.4 \times 10^{-2}$ | 1.33 | 1.28 |

The Bromo Reaction. The data for the reaction of 2,4-dinitrobromobenzene with piperidine in DMSO are listed in Tables XX through XXXI and in Figures 15 through 18. The slopes, y-intercepts, and coefficients of determination are listed in Table LVIII. The rate constants, half-lifes, and reaction orders are listed in Table LIX.

TABLE LVIII

SLOPES, Y-INTERCEPTS, AND COEFFICIENTS OF DETERMINATION FOR THE 2,4-DINITROBROMOBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNBB/ 40.0 ml cell volume | slope | | y-intercept | | CD | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | .1246 | .1823 | .990 | .995 | .9999 | .9998 |
| 0.000050 | .2721 | .4405 | .981 | .990 | .9997 | .9984 |
| 0.000070 | .3670 | .5988 | .965 | .965 | .9990 | .9978 |
| Moles of DNBB/ 20.0 ml cell volume | | | Cell 2 | | | |
| 0.000025 | .2952 | .4629 | .981 | .846 | .9998 | .9966 |
| 0.000050 | .5948 | .6874 | .974 | .973 | .9996 | .9999 |
| 0.000070 | .7856 | 1.249 | .918 | .890 | .9989 | .9965 |

The maximum recorded conductances for cell 1 and cell 2 were approximately 52 and 885 micromhos respectively, almost the same as for the chloro analog. As before, this

reaction displayed much lower conductances than the comparable values of 538 and 8,000 micromhos determined by Berkland for the bromo reaction in ethanol. The bromo compound reacted more slowly in DMSO than the chloro homolog, but was much faster than the corresponding bromo reaction in ethanol, requiring only 30 minutes at the lowest concentration in cell 1 to reach 79% completion.

TABLE LIX

RATE CONSTANT, HALF-LIFE, AND REACTION ORDER FOR THE 2,4-DINITROBROMOBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNBB/ 40.0 ml cell volume | rate k ($l\ mol^{-1}\ min^{-1}$) | | $t_{1/2}$ (min) | | $n_t$ | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | 99.7 | 145.8 | 8.02 | 5.49 | 2.01 | 2.05 |
| 0.000050 | 108.8 | 176.6 | 3.68 | 2.27 | 1.84 | 1.80 |
| 0.000070 | 104.8 | 170.9 | 2.72 | 1.67 | 2.06 | 1.90 |
| Moles of DNBB/ 20.0 ml cell volume | | | Cell 2 | | | |
| 0.000025 | 118.1 | 185.1 | 3.39 | 2.16 | 2.08 | 1.94 |
| 0.000050 | 118.8 | 137.8 | 1.68 | 1.45 | 1.94 | 2.08 |
| 0.000070 | 112.2 | 178.4 | 1.27 | .80 | 1.96 | 1.92 |

The average relative percent deviation of a measurement for cell 1 and 2 at 25.0°C was 1.70 and 0.68, while for the same cells at 35.0°C the comparable values were 0.47 and 0.79%. These are in agreement with the values determined for the chloro analog in DMSO. Cell 1 exhibits a higher relative error than cell 2. This may be due to a maximum precision limit imposed on a measurement by the physical limitation in manually balancing the bridge, which would be magnified by the mathematics when the measured conductance is less than 10 micromhos.

The y-intercepts and coefficients of determination are in general agreement with those for the chloro reaction in DMSO. The rates at 25.0°C and 35.0°C are, when averaged, 110.4 l $mol^{-1}$ $min^{-1}$ ± 7.5 and 165.7 l $mol^{-1}$ $min^{-1}$ ± 19.2 respectively. The reaction order with respect to time is close to 2.00 for these reactions also, indicating the same order as for the reaction in ethanol.

The infinity conductance ratios are listed in Table LX. At all concentrations and temperatures these ratios are slightly higher than for the chloro reaction in DMSO. The initial conductances, measured and extrapolated, appear in Table LXI. The values are consistently less than those for the chloro reaction and agreement between the measured and extrapolated values is also better. The ratios of the initial conductances are listed in Table LXII. For terms containing the .000070 concentration the ratios are

higher than those calculated for the chloro reaction in DMSO. The ratios of the infinity conductances at the two temperatures 25.0°C and 35.0°C are given in Table LXIII. These ratios are in agreement with those for the chloro reaction in DMSO, being in the range of 1.30.

TABLE LX

RATIOS OF THE INFINITY CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROBROMOBENZENE IN DMSO

| Moles of DNBB/ cell volume | 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | $C_\infty/C_\infty$ | | | |
| .000070/.000050 | 1.20 | 1.22 | 1.26 | 1.21 |
| .000050/.000025 | 1.98 | 1.91 | 1.88 | 1.87 |
| .000070/.000025 | 2.39 | 2.32 | 2.37 | 2.27 |

TABLE LXI

EXTRAPOLATED AND MEASURED INITIAL CONDUCTANCES FOR THE 2,4-DINITROBROMOBENZENE REACTION IN DMSO

| Temperature | Moles of DNBB/ cell volume | Extrapolated | | Measured | |
|---|---|---|---|---|---|
| | | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| 25.0°C | .000025 | .48[a] | 10.23 | .35 | 8.06 |
| | .000050 | .87 | 20.89 | .40 | 4.30 |
| | .000070 | 1.32 | 31.60 | 1.02 | 9.31 |
| 35.0°C | .000025 | 2.81 | 44.26 | 2.80 | 57.36 |
| | .000050 | 5.75 | 87.10 | 4.82 | 72.20 |
| | .000070 | 8.51 | 125.90 | 3.56 | 72.82 |

[a]unit: micromhos

TABLE LXII

RATIOS OF THE INITIAL CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROBROMOBENZENE IN DMSO

| Moles of DNBB/ cell volume | 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | $C_o/C_o$ | | | |
| .000070/.000050 | 1.51 | 1.51 | 1.48 | 1.48 |
| .000050/.000025 | 1.81 | 2.04 | 2.04 | 1.97 |
| .000070/.000025 | 2.75 | 3.09 | 3.02 | 2.84 |

TABLE LXIII

RATIOS OF INFINITY CONDUCTANCES AT 35.0°C TO 25.0°C FOR THE 2,4-DINITROBROMOBENZENE REACTION IN DMSO

| Piperidine, M | $C_\infty/C_\infty$ Cell 1 | Cell 2 |
|---|---|---|
| $5.0 \times 10^{-3}$ | 1.28 | 1.28 |
| $1.0 \times 10^{-2}$ | 1.22 | 1.26 |
| $1.4 \times 10^{-2}$ | 1.29 | 1.25 |

The Iodo Reaction. The data for the reaction of 2,4-dinitroiodobenzene with piperidine in DMSO are listed in Tables XXXII through XLIII and in Figures 19 through 22. The slopes, y-intercepts, and coefficients of determination are listed in Table LXIV. The rate constants, half-lifes, and reaction orders are listed in Table LXV.

The maximum conductance recorded for cell 1 was approximately 51 micromhos, and for cell 2 the maximum value was 912 micromhos. These values are about the same as those recorded for the bromo reaction. However, cell 2 for both the bromo and iodo reaction recorded a higher value than the corresponding chloro reaction. The iodo reaction was slower requiring about 90 minutes to reach 80% completion for the lowest concentration and temperature. The average relative percent deviation of a measurement for cell 1 and cell 2 at 25.0°C was 0.96 and 0.37 respectively.

For cell 1 and cell 2 at 35.0°C the corresponding values were 0.47 and 0.53%. Once again the greatest error appears in cell 1, but is less than that recorded for the chloro and bromo reactions.

TABLE LXIV

SLOPES, Y-INTERCEPTS, AND COEFFICIENTS OF DETERMINATION FOR THE 2,4-DINITROIODOBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNIB/ 40.0 ml cell volume | slope | | y-intercept | | CD | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | .02541 | .04073 | .994 | .982 | .9992 | .9994 |
| 0.000050 | .05000 | .07848 | 1.004 | .992 | .9997 | .9999 |
| 0.000070 | .06910 | .1090 | .983 | .982 | .9997 | .9996 |
| Moles of DNIB/ 20.0 ml cell volume | | | | | | |
| | | | Cell 2 | | | |
| 0.000025 | .04833 | .07262 | .997 | .994 | .9999 | .9999 |
| 0.000050 | .1032 | .1478 | .990 | .987 | .9998 | .9999 |
| 0.000070 | .1392 | .2099 | .961 | .988 | .9989 | .9993 |

The y-intercepts and coefficients of determination are internally more consistent and closer to the theoretical value of 1.00 than the chloro or bromo reaction, though the differences are rather small and within the range of values for the chloro reaction by Frank and the bromo and iodo

reactions in ethanol by Berkland.

TABLE LXV

RATE CONSTANT, HALF-LIFE, AND REACTION ORDER FOR THE 2,4-DINITROIODOBENZENE REACTION IN DMSO AT VARIOUS CONCENTRATIONS AND TEMPERATURES

| Moles of DNIB/ 40.0 ml cell volume | rate k (l $mol^{-1}$ $min^{-1}$) | | $t_{\frac{1}{2}}$ (min) | | $n_t$ | |
|---|---|---|---|---|---|---|
| | 25.0°C | 35.0°C | 25.0°C | 35.0°C | 25.0°C | 35.0°C |
| | | | Cell 1 | | | |
| 0.000025 | 20.33 | 32.59 | 39.40 | 24.55 | 2.00 | 2.00 |
| 0.000050 | 20.33 | 31.39 | 20.00 | 12.74 | 2.05 | 1.86 |
| 0.000070 | 19.74 | 31.14 | 14.42 | 9.18 | 1.92 | 1.87 |
| Moles of DNIB/ 20.0 ml cell volume | | | Cell 2 | | | |
| 0.000025 | 19.33 | 29.05 | 20.80 | 13.77 | 1.96 | 1.97 |
| 0.000050 | 20.64 | 29.56 | 9.71 | 6.77 | 1.94 | 1.98 |
| 0.000070 | 19.88 | 29.99 | 7.18 | 4.76 | 1.85 | 1.89 |

The average reaction rates for the iodo reaction at 25.0°C and 35.0°C are respectively 20.04 l $mol^{-1}$ $min^{-1}$ ± 0.48 and 30.62 l $mol^{-1}$ $min^{-1}$ ± 1.32. The individual rates have considerably better precision (5 to 10 times) than the chloro or bromo reactions. This may be due in part to the slower rate of reaction which permitted more points to be used in the calculation of the slope and intercept. The

reaction order with respect to time is close to the theoretical value of 2.00.

The infinity conductance ratios are listed in Table LXVI and are in agreement with the values for the chloro and bromo reactions. The initial conductances, measured and extrapolated, are given in Table LXVII. The ratios of the extrapolated initial conductances are listed in Table LXVIII. These values are consistent with those for the chloro and bromo reactions. The ratios of the infinity conductances at 35.0°C to 25.0°C are given in Table LXIX. The ratio of 1.20 is slightly lower than the values obtained for the chloro and bromo reactions and is less than the ratio of 1.50 for the two reaction rates at the temperatures examined.

TABLE LXVI

RATIOS OF THE INFINITY CONDUCTANCES FOR VARIOUS CONCENTRATIONS OF 2,4-DINITROIODOBENZENE IN DMSO

| Moles of DNIB/ cell volume | 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | $C_\infty/C_\infty$ | | | |
| .000070/.000050 | 1.32 | 1.30 | 1.29 | 1.27 |
| .000050/.000025 | 1.98 | 2.00 | 1.98 | 1.94 |
| .000070/.000025 | 2.63 | 2.61 | 2.56 | 2.46 |

TABLE LXVII

EXTRAPOLATED AND MEASURED INITIAL CONDUCTANCES FOR THE 2,4-DINITROIODOBENZENE REACTION IN DMSO

| Temperature | Moles of DNIB/ cell volume | Extrapolated | | Measured | |
|---|---|---|---|---|---|
| | | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| 25.0°C | .000025 | .50[a] | 8.51 | .43 | 8.83 |
| | .000050 | .78 | 12.88 | .53 | 10.75 |
| | .000070 | 1.05 | 16.85 | 1.09 | 16.84 |
| 35.0°C | .000025 | 1.25 | 19.50 | 1.38 | 17.90 |
| | .000050 | 1.75 | 23.44 | 1.45 | 22.40 |
| | .000070 | 2.04 | 31.23 | 2.03 | 30.46 |

[a]unit: micromhos

TABLE LXVIII

RATIOS OF THE INITIAL CONDUCTANCES FOR DIFFERENT CONCENTRATIONS OF 2,4-DINITROIODOBENZENE IN DMSO

| Moles of DNIB/ cell volume | 25.0°C | | 35.0°C | |
|---|---|---|---|---|
| | Cell 1 | Cell 2 | Cell 1 | Cell 2 |
| | $C_o/C_o$ | | | |
| .000070/.000050 | 1.35 | 1.31 | 1.17 | 1.33 |
| .000050/.000025 | 1.56 | 1.51 | 1.40 | 1.20 |
| .000070/.000025 | 2.10 | 1.98 | 1.63 | 1.60 |

TABLE LXIX

RATIOS OF THE INFINITY CONDUCTANCES AT 35.0°C to 25.0°C FOR THE 2,4-DINITROIODOBENZENE REACTION IN DMSO

| Piperidine, M | $C_\infty/C_\infty$ Cell 1 | Cell 2 |
|---|---|---|
| $5.0 \times 10^{-3}$ | 1.21 | 1.24 |
| $1.0 \times 10^{-2}$ | 1.21 | 1.20 |
| $1.4 \times 10^{-2}$ | 1.19 | 1.18 |

The decreasing initial conductance, extrapolated or measured, with the change from chloride to iodide should be expected to match a decrease in the infinity conductances, if there were some error in solution preparation, or if an element effect was influencing ion-pair formation or the conductivity of the reactants and hence the measured conductance. Since the initial conductances decrease while the infinity conductances increase in the order $Cl<Br\leq I$, the change in conductance observed when 2,4-dinitrochlorobenzene was dissolved in DMSO is probably due to reaction with one of the decomposition products rather than the formation of a charged complex. The bromo and iodo compounds would normally be expected to be less reactive than the chloro analog. This is indicated by the higher infinity conductances and closer agreement between the infinity measurements for the bromo and iodo reactions as against that for the chloro reaction.

It is also possible, however, that 2,4-dinitrophenylpiperidine adsorbed on the platinum black electrode surface could be going back into solution, thereby accounting for the increase in solution color observed. Likewise, absorbed salt might also account for the increase in conductance.

Finally, it has been suggested by Dr. J. G. Lindberg of the Department of Chemistry that 2,4-dinitrohalobenzene may be ionizing to produce small amounts of 2,4-dinitrophenyl carbanions and positively charged halide ions. These halide cations could be solvated by the negative charge on the DMSO oxygen. Such an ionization could also account for the increase in color intensity observed.

Energy of Activation and Entropy Relationships. The energy required to form the activated complex is termed the energy of activation. Equation (43) was used to calculate the energy of activation for the chloro, bromo, and iodo analogs in DMSO. Only two temperatures were examined in view of the constraints imposed by the speed of the reaction and the physical properties of the solvent. With only two temperatures it is not necessary to plot the log of the rate against the reciprocal of the temperature in degrees Kelvin, and instead, direct substitution into the two point equation becomes possible. The energy of activation for the chloro reaction was 5.70 kcal and for the bromo and iodo reactions the values were 7.21 and 7.52 kcal,

respectively.

Equation (47) was employed to calculate the entropy for each of the reaction analogs. The values for the chloro, bromo and iodo reactions were -33.65, -26.88, and -28.58 cal $deg^{-1}$ $mol^{-1}$ respectively. The values for the energy of activation, entropy, and rate constants are listed in Table LXX. Any of these values can be used to determine the reaction series order for 2,4-dinitrohalobenzene with piperidine in DMSO. Thus in terms of rate constants, the reaction series becomes Cl>Br>>I, while in terms of activation energies the difference between the bromo and iodo analogs diminishes yielding the reaction series Cl>Br$\geq$I. This might be interpreted as a type of solvent leveling effect with the reaction approaching the point of reversing as has been observed for some $S_N1$ reactions (8).

TABLE LXX

AVERAGE RATE CONSTANTS, ENERGIES OF ACTIVATION, AND ENTROPIES FOR THE REACTION OF 2,4-DINITROHALOBENZENE WITH PIPERIDINE IN DMSO

| Halogen group | k(l $mol^{-1}$ $min^{-1}$) 25.0°C | 35.0°C | $\Delta E^{\dagger}$(Kcal) | $\Delta S^{\dagger}$(cal $deg^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| Chloro- | 142.8 | 195.2 | 5.70 | -33.65 |
| Bromo- | 111.2 | 165.7 | 7.21 | -26.88 |
| Iodo- | 20.04 | 30.62 | 7.72 | -28.58 |

The reaction series order in terms of entropies is Cl>I≥Br, which represents an anomaly with respect to the order indicated by the rate constants or activation energies. The values determined by Frank and Berkland are listed in Table LXXI. A similar discrepancy for the reaction order in terms of entropies as against rate constants and activation energies was reported by Berkland. The reaction order as indicated by these last two parameters is Cl≥Br>>I.

TABLE LXXI

AVERAGE RATE CONSTANTS, ENERGIES OF ACTIVATION, AND ENTROPIES FOR THE REACTION OF 2,4-DINITROHALOBENZENE WITH PIPERIDINE IN ETOH

| | $k(l\ mol^{-1}\ min^{-1})$ | | | | |
|---|---|---|---|---|---|
| Halogen | 0.1°C | 25.0°C | 40.0°C | $\Delta E^{\dagger}$(kcal) | $\Delta S^{\dagger}$(cal $deg^{-1}$ $mol^{-1}$) |
| Chloro- | .3188 | 1.691[a] | 4.423 | 11.29[b] | -21.56[c] |
| Bromo- | .2748 | 1.588 | 4.216 | 11.69 | -20.38 |
| Iodo- | .0559 | 0.360 | 1.007 | 12.37 | -20.93 |

[a]The average rate is the average of the rates determined by Frank, Berkland and the present study.

[b]Adjusted using the recalculated rate constant at 25.0°C.

[c]These values are calculated using $\Delta H^{\dagger}$, where $\Delta H^{\dagger} \simeq \Delta E_{exp} - RT$.

Since this inconsistency in the bromo and iodo entropy values appears for both ethanol and DMSO, it serves as additional evidence that the same basic type of $S_NAr_2$ mechanism is probably operating when the solvent is changed from a polar to dipolar aprotic solvent. It is possible that the conductance method is magnifying some physical parameter associated with conductance properties of the two halogens. However, the study by Youngberg indicates that the conductometric method of following the reaction of 2,4-dinitrohalobenzene with a secondary amine yields a rate constant of higher precision than either the spectrophotometric method or titrimetric method. The question of accuracy still remains unanswered, but there appears to be no significant interference with the reaction as a result of using conductance as the measured property.

The values obtained by Suhr (68) for the reaction of 4-nitrohalobenzene with piperidine in DMSO are listed in Table LXXII. The difference between the entropy values for the chloro, bromo, and iodo analogs, while spaced rather closely and lower than the bromo and iodo values of this study, nevertheless display a similar reversal of the bromo and iodo values.

The entropy values for the chloro analogs of both systems (DNXB and NXB) are about the same, while the activation energies are approximately one-third lower for the 2,4-dinitrohalobenzene reactions. The energy of activation

for this system is lowered significantly when the solvent is changed from ethanol to DMSO and the chloro analog is affected the most.

TABLE LXXII

AVERAGE RATE CONSTANTS, ENERGIES OF ACTIVATION, AND ENTROPIES FOR THE REACTION OF 4-NITROHALOBENZENE WITH PIPERIDINE IN DMSO

| Halogen | $k(l\ mol^{-1}\ min^{-1})$[a] 50.0°C | 75.0°C | $\Delta E^{\dagger}$(kcal) | $\Delta S^{\dagger}$(cal $deg^{-1}\ mol^{-1}$) |
|---|---|---|---|---|
| Fluoro- | 1.64 | 3.66 | 7.15 | -37.44 |
| Chloro- | $3.96 \times 10^{-3}$ | $1.58 \times 10^{-2}$ | 12.35 | -33.30 |
| Bromo- | $4.80 \times 10^{-3}$ | $1.89 \times 10^{-2}$ | 12.25 | -33.25 |
| Iodo- | $1.10 \times 10^{-3}$ | $4.74 \times 10^{-2}$ | 13.02 | -33.28 |

[a]These values were determined by Suhr (68) and reported in units of $k \times 10^{6}$ $sec^{-1}$ $mol^{-1}$ l. Here they have been translated to the units used in the present study for the purpose of comparison.

The limiting conductances of halides, excluding fluoride, at 25.0°C in protic and aprotic solvents are listed in Table LXXIII. The conductance behavior in ethanol and DMSO seems to reflect the influence of DMSO on the chloro analog and the activation energy. Table LXXIV compares the influence of solvent on the system examined in this study and that investigated by Suhr. Thus in relative terms DMSO produces a greater increase in rate for 4-nitrohalobenzene than 2,4-dinitrohalobenzene as indicated by

the log $k_{DMSO}/k_{ETOH}$ values. In fact the influence of DMSO on each system is in the opposite direction decreasing in the order Cl>Br>I for DNXB and increasing in the order Cl<Br<I for NXB.

TABLE LXXIII

LIMITING IONIC CONDUCTANCES OF HALIDE IONS IN SELECTED PROTIC AND APROTIC SOLVENTS AT 25.0°C

| Halide Ion | $\lambda_o$(DMSO) | $\lambda_o$(ETOH) | $\lambda_o$(MEOH) | $\lambda_o$(DMF) | $\lambda_o$($H_2O$) |
|---|---|---|---|---|---|
| Chloride | 36.3 | 24.3 | 52.4 | 55.1 | 76.3 |
| Bromide | 24.2 | 26.0 | 56.5 | 53.6 | 78.4 |
| Iodide | 23.8 | 28.8 | 62.7 | 52.3 | 76.8 |

Reference: Parker (73)

A plot of log $k_{DMSO}/k_{ETOH}$ ratios at 50.0°C against the carbon-halogen (C-X) bond lengths (Figures 24 and 25) shows the strong influence of DMSO on the iodo analog of the DNXB and NXB systems. The curves for the two different systems have opposite slopes. The relationship between C-X bond length and ratios for the DNXB system appears to be rather regular which is contrary to the more dramatic change displayed by the NXB system. The exact significance of this is not immediately obvious. However, in addition to steric factor differences, the charge densities on the leaving groups in the two transition states (Figure 6) would

be different due to the electron withdrawing effect of the ortho-nitro.

TABLE LXXIV

HYDROGEN BONDING ACTIVITY COEFFICIENT OF THE ANION

| Halide leaving group | C-X bond Length[a] A | log $k_{DMSO}/k_{ETOH}$ 2,4-dinitrohalobenzene 25.0°C[b] | 2,4-dinitrohalobenzene 50.0°C[c] | 4-nitrohalobenzene 25.0°C[d] | 4-nitrohalobenzene 50.0°C[e] |
|---|---|---|---|---|---|
| Chloride | 1.67 | 1.926 | 1.628 | 2.248 | 1.900 |
| Bromide | 1.86 | 1.845 | 1.579 | 2.271 | 1.944 |
| Iodide | 2.08 | 1.746 | 1.470 | 3.080 | 2.593 |

[a]Reference (100): measured bond lengths for phenylhalides.

[b]Calculated using data listed in Tables LXX and LXXI.

[c]Extrapolated using data in Tables LXX and LXXI.

[d]Extrapolated by ratio using the data in this table.

[e]Calculated using the data reported in Table LXXII$_{-3}$ and reported values in ethanol at 50.0°C (68): F=8.4 x $10^{-3}$; Cl=4.98 x $10^{-5}$: 3.96 x $10^{-5}$; Br=5.46 x $10^{-5}$; I=2.82 x $10^{-6}$. These rates are in 1 $mol^{-1}$ $min^{-1}$. They were reported as 1 $mol^{-1}$ $sec^{-1}$ x $10^{6}$. The chloro value 4.98 x $10^{-5}$ was used. At 50.0°C, the ratio for fluoride is 2.292.

Viewing the reaction of Figure 1 in terms of HSAB, it can be said that hard anions experience hard interactions with hard solvents, and, conversely, soft anions display strong interactions with soft solvents. Given that protic

solvents are hard and dipolar aprotic solvents are soft; the overall effect of DMSO is to make dinitrohalobenzene, piperidine, and the resulting transition state softer.

Since dinitrohalobenzene is a soft substrate, a strong interaction with DMSO can be expected as indicated in Table LXX. Piperidine is a borderline nucleophile with respect to hardness and softness, and considering its ring structure, a strong interaction with DMSO would not be expected. Hydrogen bonding between the amine and DMSO does not appear to be a significant factor (61). Nevertheless, the methyl groups of DMSO should provide adequate solvation of the amine ring structure, and the orientation of this solvation might tend to shield the softness of the nitrogen from the DMSO sulfur-oxygen double bond.

The product 2,4-dinitrophenylpiperidine should be softer than dinitrohalobenzene substrate because of the possibility of extended conjugation using the unpaired electrons of the amine nitrogen.

Looking at the transition state (Figure 6) as an acid-base complex, the hard halides would not be expected to interact well with the softer acid-base complex. The reactivity series in ethanol, F>>Cl$\geq$Br>>I, or in DMSO, Cl$\geq$Br>>I, for the halogens shows that iodine being the softest member of the halogen family interacts the most strongly with the soft dinitrophenyl group and is the hardest to displace.

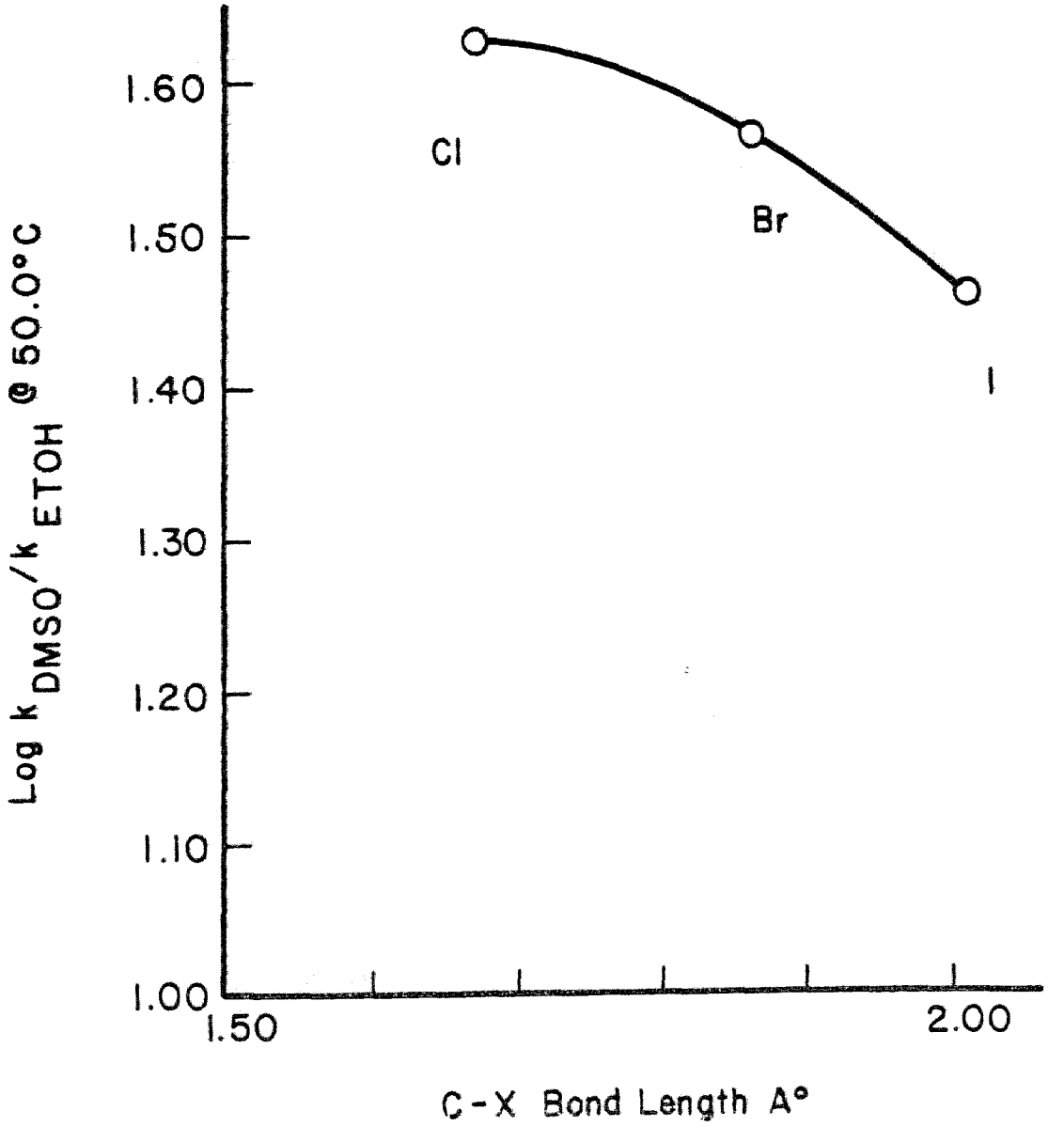



Figure 24. Carbon-halogen bond length versus the hydrogen bonding activity coefficient of the halide leaving group for 2,4-dinitrohalobenzene (ref. this work).

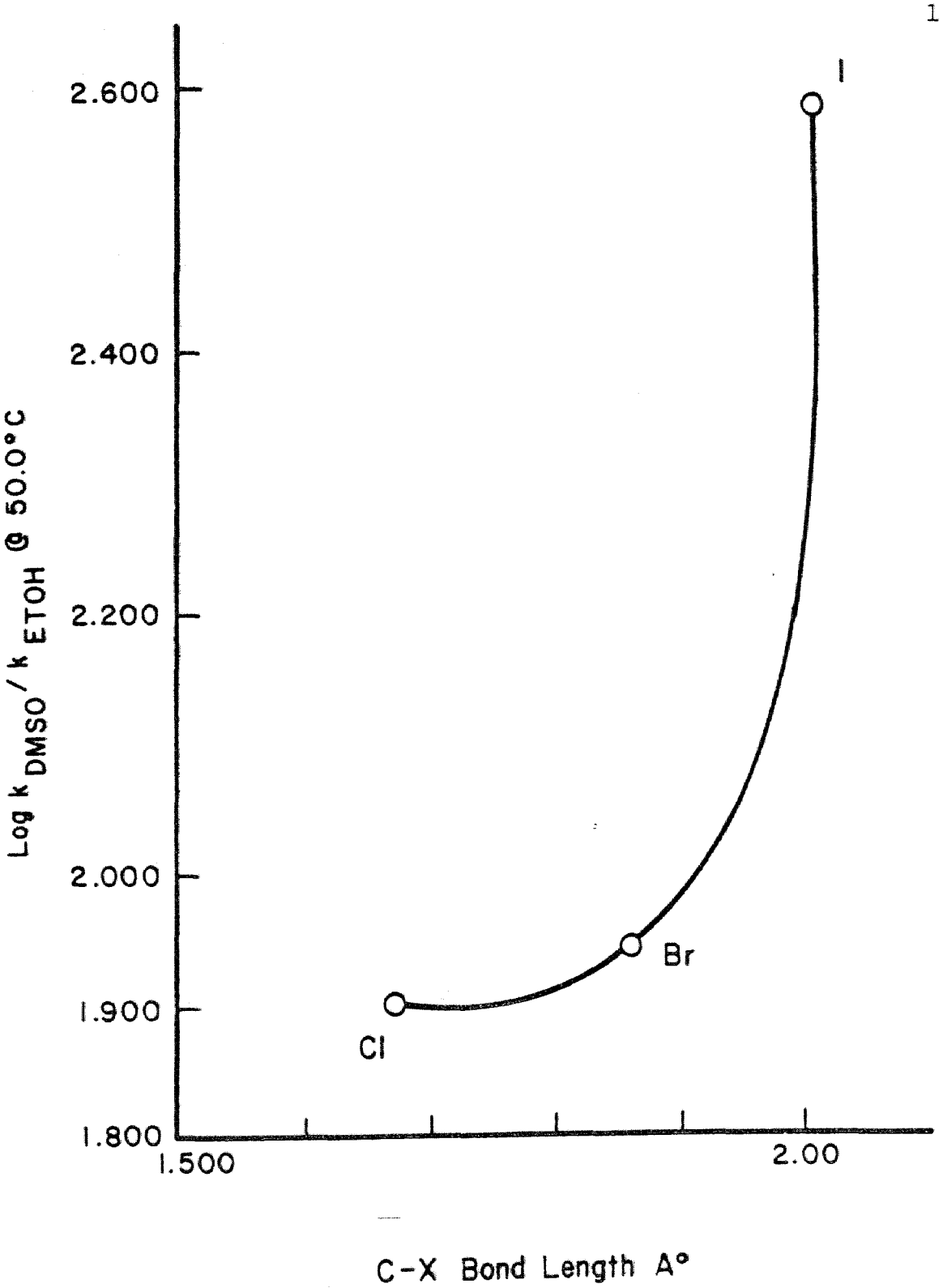



Figure 25. Carbon-halogen bond length versus the hydrogen bonding activity coefficient of the halide leaving group for 4-nitrohalobenzene (ref. 68).

Even if the proton is removed from the piperidinium nitrogen before the halide leaves, the favoring of soft-soft interactions between the unshared electrons of the amine nitrogen and the resonance of the 2,4-dinitrophenyl group would be expected to exceed the hard-soft interactions of the halide and 2,4-dinitrophenyl group. A similar analysis can be applied to 4-nitrohalobenzene and piperidine. In this case, the slower rate of reaction with piperidine as compared to the dinitro-compound is due to the decreased softness of the mononitro-substituted benzene.

The relative increases in rate on changing solvent from ethanol to DMSO for both the mono- and dinitro-systems are approximately the same for the chloro and bromo analogs. For the iodo analog, however, a greater relative increase was observed for the 4-nitro compound than for the 2,4-dinitro compound. Since the iodo reaction is slower than the chloro or bromo analogs, the precision should be higher, irrespective of whether a conductometric or spectrophotometric method of following the reaction is employed. The close agreement between the values obtained for the iodo reaction of this study indicate good precision.

Assuming, as indicated above, that a specific solvation is occurring, then the enhanced rate of 2,4-dinitroiodobenzene and 4-nitroiodobenzene when the solvent is changed from protic to dipolar aprotic may be interpreted as a stabilization of the transition state. Hepalute

and Robertson (101) have suggested that, as a useful working hypothesis, the transition state be considered as that point at which solvent-substrate interactions equal solvent-solvent interactions. Such a stabilized transition state would tend to favor the stronger interaction of the larger $I^-$ with the solvent DMSO. This may be a factor in the large relative increase of 350 observed by Suhr for iodo-4-nitrobenzene.

If one or more DMSO molecules are linking the positive and negative centers in the transition state, the orientation would probably be influenced by the nitro group in the ortho position. For the DNXB system the orientation of a specific solvation by a DMSO molecule would probably be between the reaction site entering or leaving group and the neighboring nitro group as proposed by Bernasconi (61). The higher entropies for the iodo and bromo analogs of this system as against the NXB system could be interpreted as supporting this explanation, since the arrangement of two or more DMSO molecules between the positive and negative centers of the NXB transition state would be expected to lower the entropy of the system.

As indicated by Parker (8) when solubilities are known for the substrates of this study and that of Suhr (66, 67,68), calculations based on the extrathermodynamic assumptions mentioned in the literature review will be possible.

Unfortunately, there have been no rate determinations

using the spectrophotometric or titrimetric methods for the system investigated in this study, and no values are reported in the literature, which would allow comparison with the values determined in this study. Since a rate increase of approximately 100 could be expected for this reaction based on the work of Suhr and the precision was within the range of the equipment and also in agreement with the precision of measurements for the same system in ethanol, the rates determined in DMSO appear to be internally consistent. However, whether the apparent opposite trend in the influence of DMSO on the relative reactivity of the halogens in the series is real and due to some difference in mechanism or a catalytic affect by DMSO, or is the result of spurious measurements, remains unclear.

The incorporation of appropriate digital control for continuous bridge balancing would facilitate the collection of data. Such a continuously balanced system could by means of a suitable transducer be connected to any of the various desk top computers available for on-line data reduction and analysis.

The cell itself could be designed along the lines, as suggested by Frank and Berkland, of a Wolin U tube which would result in a closed system. The advantages of such a system would be more rapid mixing of the reactants and minimum exposure of the system under study to air or moisture. Also, since the cell would not have to be manipulated,

a higher precision temperature bath system could be designed.

The design and construction of this apparatus would probably result in measurements of greater precision and relieve the tedium of data collection for certain types of reaction mechanism studies. Aside from the relative advantages of such technical improvements, the conductance method might be applied to a broader range of reaction types and temperatures.

For example, it may be possible to determine the amount of DMSO decomposition products present after purification by developing a standard calibration curve (i.e. reaction rates with known amounts of DNCB). However, time did not permit investigation of this during the course of this study. Furthermore, the possibility of using the conductance method to measure $SN_1$ reactions in dipolar aprotic solvents offers an area for study. The mathematics relating conductance changes to reaction rate would, of course, be more complex than that of uncharged molecule reactions, but it may be possible to employ some type of differential analysis technique.

Differential techniques have already been applied to several types of quantitative organic determinations. Analysis for which this type of conductometric determination have been investigated include:

1) Quantitative determination of organic halides in DMSO (102).

2) Rapid analysis of binary amine mixtures by differential reaction rates (103).

3) Conductometric analysis of binary amine mixtures (104).

4) Conductometric determination of carbonyl compounds (105).

# LITERATURE CITED


1. Laidler, K. J., Chemical Kinetics, 2nd ed., McGraw-Hill, Inc., New York, 1965, p. 2.

2. Frank, C. O., M.A. Thesis, Drake University, Des Moines, Iowa, 1964.

3. Berkland, T. R., M.A. Thesis, Drake University, Des Moines, Iowa, 1966.

4. Jacob, F. E., and T. R. Berkland, Proc. Iowa Acad. Sci., 74, 47 (1967).

5. Bunnett, J. F., and H. D. Crockford, J. Chem. Educ., 32, 556 (1956).

6. Frost, A. A., and R. G. Pearson, Kinetics and Mechanism, 2nd ed., John Wiley & Sons, New York, 1961, p. 37.

7. Parker, A. J., Quart. Rev. (London), 16, 163 (1962).

8. Parker, A. J., Chem. Rev., 69, 1 (1969).

9. Davis, M. M., Acid Base Behavior in Aprotic Organic Solvents, National Bureau of Standards Monograph 105, U.S. Government Printing Office, Washington, D.C., 1968.

10. Dack, M. R. J., Chem. Techn., 108 (Feb. 1971).

11. Cajori, F., A History of Physics, The Macmillan Co., New York, 1917, p. 135.

12. Ihde, A. J., The Development of Modern Chemistry, Harper and Row, New York, 1974, pp. 131-132.

13. Moore, W., Physical Chemistry, Prentice Hall, Inc., New York, 1955, p. 437.

14. Cajori, F., A History of Physics, The Macmillan Co., New York, 1917, pp. 217-218.

15. Quincke, G., J. Amer. Chem. Soc., 25, 207 (1872).

16. Muir, M. M. P., A History of Chemical Theories and Laws, John Wiley & Sons, New York, 1909, p. 331.

17. Samuel Glasstone, An Introduction to Electrochemistry, D. Van Nostrand Co., Inc., New York, 1942, pp. 32-35.

18. Cajori, F., A History of Physics, The Macmillan Co., New York, 1917, p. 232.

19. Jones, G., and D. Bollinger, J. Amer. Chem. Soc., 57, 280 (1935).

20. Jones, G., and D. Bollinger, J. Amer. Chem. Soc., 53, 411 (1931).

21. Horoaka, F., and E. E. Mendenhall, J. Chem. Educ., 16, 239-241 (1939).

22. Ihde, A. J., The Development of Modern Chemistry, Harper and Row, New York, 1964, pp. 406-407.

23. Negreano, J. Amer. Chem. Soc., 54, 1025 (1888).

24. Price, T. S., J. Amer. Chem. Soc., 79, 303 (1901).

25. Rivett, A., and N. Sidgwick, J. Amer. Chem. Soc., 97, 677 (1898).

26. Greenberg, D. B., J. Chem. Educ., 34, 140 (1962).

27. Cody, H. P., and H. O. Lictenwalter, J. Amer. Chem. Soc., 35, 1434 (1913).

28. Maron, S. H., and V. K. Lamer, J. Amer. Chem. Soc., 61, 692 (1939).

29. Gucker, F. T., and W. B. Meldro, Physical Chemistry, The American Book Co., New York, 1944, p. 281.

30. Chesick, J., and A. Patterson, Jr., J. Chem. Educ., 37, 242 (1960).

31. Jones, B., and D. J. Worsfold, Nature, 167, 1072 (1951).

32. Norris, J. F., and A. A. Morton, J. Amer. Chem. Soc., 50, 1795 (1928).

33. H. J. Opstall, Rec. Trav. Chim. Pays-Bas, 53, 901-911 (1933); Chem. Abstr., 28, 26 (1934).

34. Hammond, G. S., and L. R. Parks, J. Amer. Chem. Soc., 77, 340-343 (1955).

35. Singh, A., and D. H. Peacock, J. Phys. Chem., 40, 669-678 (1958).

36. Parks, L. R., G. S. Hammond, and F. Hawthorne, J. Amer. Chem. Soc., 77, 2903-2904 (1955).

37. Bunnett, J. F., and R. J. Morath, J. Amer. Chem. Soc., 74, 5165 (1952).

38. Berliner, E., J. Amer. Chem. Soc., 74, 1574-1579 (1952).

39. Bunnett, J. F., and G. T. Davis, J. Amer. Chem. Soc., 76, 3011-3015 (1954).

40. Adeniran, M. A., C. W. L. Bevon, and J. Hirst, J. Chem. Soc., 5868-5872 (1963).

41. Greizstein, W., R. A. Bonelli, and J. A. Brieux, J. Amer. Chem. Soc., 84, 1026-1032 (1962).

42. Brieux, J. A., and V. Beulofew, Chem. Ind. (London), 971 (1951).

43. Bunnett, J. F., and R. J. Morath, J. Amer. Chem. Soc., 77, 5051-5055 (1955).

44. Hawthorne, B. M. F., J. Amer. Chem. Soc., 76, 6358-6360 (1954).

45. Bunnett, J. F., J. Amer. Chem. Soc., 79, 5969-5974 (1957).

46. Beltam, P., and M. Simonetto, Gazz. Chim. Ital., 92, 351-364 (1962); Chem. Abstr., 55, 6478 (1961).

47. Berliner, E., M. Quinn, and P. J. Edgerton, J. Amer. Chem. Soc., 72, 5305-5308 (1950).

48. Brower, K. R., and E. D. Amstutz, J. Org. Chem., 18, 1075-1078 (1953).

49. Youngberg, L. E., M. A. Thesis, Drake University, Des Moines, Iowa, 1974.

50. Kharasch, N., and B. S. Thyagarajin, "Quarterly Reports on Sulfur Chemistry," I, No. 1, (March, 1966).

51. Agami, C., Bull. Soc. Chim. Fr., 5th series, 1021-39 (1965).

52. Parker, A. J., "Advances in Organic Chemistry," Vol. 5, John Wiley & Sons, New York, 1965, pp. 1-46.

53. Martin, D., A. Waise, and H. J. Niclas, Angew. Chem. Int. Ed., 6, 318 (1967).

54. Davis, M. M., Acid-base Behavior in Aprotic Organic Solvents, National Bureau of Standards Monograph 105, U.S. Government Printing Office, Washington, D.C., 1968, p. 17.

55. Ritchie, C. D., and A. L. Pratt, J. Amer. Chem. Soc., 86, 1571 (1964).

56. Neng-Ping, Y., and D. N. Bennion, J. Electrochem. Soc.: Electrochem. Sci., 118 (7), 1105 (July, 1971).

57. Miller, J., and A. J. Parker, J. Amer. Chem. Soc., 83, 117 (1961).

58. Crown Zellerbach Corp., Chemical Products Division, Dimethyl Sulfoxide; Technical Bulletin, Camas, Washington, 1966, p. 1.

59. Suhr, H., Z. Naturforsch., 19b, 171-172 (1964).

60. Bader, H., A. R. Hansen, and F. J. McCarthy, J. Org. Chem., 31, 2319-2321 (1966).

61. Bernasconi, C. F., M. Kaufman, and H. Zollinger, Helv. Chim. Acta., 49, 2563-2570 (1966).

62. Calligaris, M., G. Illuminati, and G. Mariano, J. Amer. Chem. Soc., 89, 3518-3521 (1967).

63. Kingsury, C. A., J. Org. Chem., 29, 3262-3270 (1964).

64. Genel, F., G. Illuminati, and G. Marino, J. Amer. Chem. Soc., 89, 3516-3518 (1967).

65. Illuminati, G., G. Marino, and G. Slecter, J. Amer. Chem. Soc., 89, 3510-3515 (1967).

66. Suhr, H., Ber. Bunsenges. Physik. Chem., 67 (9), 893-898

67. Suhr, H., and H. Grube, Ber. Bunsenges. Physik. Chem., 70 (5), 544-50 (1966) (Ger.).

68. Suhr, H., Chem. Ber., 97, 3277 (1964) (Ger.).

69. Brady, O. L., and F. R. Cropper, J. Chem. Soc. (London), 507 (1950).

70. Bunnett, J. F., and R. H. Garst, J. Amer. Chem. Soc., 87, 3875 (1965).

71. Ross, S. D., Prog. Phys. Org. Chem., I, 31 (1963).

72. Laidler, K. J., Chemical Kinetics, 2nd ed., McGraw-Hill, Inc., New York, 1965, p. 252.

73. Parker, A. J., in Advances in Physical Organic Chemistry, 5, 173 (1967).

74. Alexander, R., and A. J. Parker, J. Amer. Chem. Soc., 89, 5549 (1967).

75. Pearson, R. G., in Survey of Progress in Chemistry, A. Scott, ed., 5, Academic Press, New York, 1969, pp. 28-29.

76. Pearson, R. G., J. Chem. Educ., 45, 581, 643 (1968).

77. Pearson, R. G., J. Amer. Chem. Soc., 89, 1827 (1967).

78. Pearson, R. G., J. Amer. Chem. Soc., 90, 319 (1968).

79. Arhland, Z., J. Chu and N. R. Davis, Quart. Rev. (London), 12, 265 (1958).

80. Bennett, G. M., and I. H. Vernon, J. Chem. Soc., 1783 (1938).

81. Bunnett, J. F., and R. M. Conner, J. Org. Chem., 23, 305-306 (1958).

82. Industrial Instruments Inc., Instruction Manual, Cedar Grove, New Jersey, 1965.

83. Fischer Scientific Co., Fischer Modern Laboratory Appliances, New York, 1964.

84. Daniels, F., and R. A. Alberty, Physical Chemistry, 3rd ed., John Wiley & Sons, New York, 1967, pp. 386-391.

85. Glasstone, S., and D. Lewis, Elements of Physical Chemistry, D. Van Nostrand Co., New York, 1960, pp. 429-433.

86. Ouellette, R. J., Can. J. Chem., 43, 707 (1965).

87. Bunnett, J. F., and C. F. Bernasconi, J. Amer. Chem. Soc., 87, 5209 (1965).

88. Körner, W., Gazz. Chim. Ital., 4, 323 (1874).

89. Laidler, K. J., Chemical Kinetics, 2nd ed., McGraw-Hill Co., New York, 1965, pp. 3-4.

90. Miller, J., Aromatic Nucleophilic Substitution, Elsevier Co., New York, 1968, p. 21.

91. Young, H., Statistical Treatment of Experimental Data, McGraw-Hill Co., New York, 1962, pp. 121, 15-18.

92. Chou, Y., Probability and Statistics for Decision Making, Holt, Rinehart and Winston Inc., New York, 1972, p. 477.

93. Dean, R. B., and Dixon, Anal. Chem., 23, 636 (1951).

94. Laidler, K. J., Chemical Kinetics, 2nd ed., McGraw-Hill, Inc., New York, 1965, pp. 16-17, 53.

95. Noyes, A. A., The Electrolytic Conductivity of Aqueous Solutions, Carnegie Institute of Washington, D.C., 1970, p. 122.

96. Youmans, H. C., "Statistics for Chemistry," Charles E. Merrill Publishing Co., Columbus, Ohio, 1973, pp. 27-38, 118-119.

97. Kolthoff, I. M., and T. B. Reddy, Inorg. Chem., 1, 189 (1962).

98. Traynelis, U. J., and W. L. Hergenrother, J. Org. Chem., 29, pp. 221-222 (1964).

99. "Handbook of Chemistry and Physics," 47th ed., Chemical Rubber Co., Cleveland, Ohio, 1966, p. c-554(s326).

100. Chemical Society Burlington House London, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, Chem. Soc. (London), 1958, pp. M194, 195, 196.

101. Hepalute, L., and T. Robertson, J. Amer. Chem. Soc., 88, 1911 (1966).

102. Vinson, J. A., and J. S. Fritz, Anal. Chem., 40, 2194 (1968).

103. Grienke, R. A., and H. B. Mark, Jr., Anal. Chem., 38, 1001 (1966).

104. Grienke, R. A., and H. B. Mark, Jr., Anal. Chem., 39, 1572 (1967).

105. Grienke, R. A., and H. B. Mark, Jr., Anal. Chem., 38, 340 (1966).

# APPENDIX I

A grant for computer time provided by the Graduate School made it possible to utilize the facilities of the Dial Computer Center during the course of this study. The following computer program was written to reduce the experimental data and print out the data tables. In addition to the calculations described in the calculation section, the program also calculates specific and equivalent conductances for the salt concentrations at each time. The two subroutines and the plotting program were adapted from the standard user linear regression program of the Center.

The program is written in Fortran IV language. The main program is preceded by a list of the variables and followed by the two subroutines.

## List of Variables

```
C     DESCRIPTION OF VARIABLES
C     CELL is the conductance cell; X is the independent
      variable for linear regression; Y is the dependent
      variable for linear regression; FMT is for the plot
      format; TITLE is an 80 unit line for the plot title.
C     M is the number of observations at each time; TIME is
      the time the observation was made; CT is the con-
      ductance measured at time (t) for each run; MEAN is
      the mean of the conductances recorded at time (t) for
      several runs; STNDEV is the standard deviation of the
      conductance value for several runs at time (t); STDVMN
      is the standard deviation for the mean for a small
      number of observations; DEVTM is the deviation in time
      for values less than 1 minute; DCDT is the change in
      conductance with respect to time; DEVCT is the change
      in conductance per change in time; DEVCT2 is a counter
      for DEVCT; W is the list of values used to calculate
      95% confidence intervals for conductance values at
      time (t); SCT stands for a single conductance run;
      CONRT is the conductance ratio; CXTOCA is the
```

concentration of x to a; CPIPX is the concentration of the piperidinium halide salt at time (t); RCPIPX is the square root of CPIPX; LCPIPX is the log of CPIPX; lALEFT is the concentration of a remaining at time (t); LALEFT is the log of lALEFT; KAPPA is the specific conductance of the salt formed and other species present at time (t); KAPPAl is the specific conductance of only the salt formed; Lamda is the equivalent conductance of the salt formed and reactants at time (t); CI95 is the 95% confidence interval of the average conductance at time (t); LAMDAl is the equivalent conductance of only the salt formed; LLAMDA is the log of LAMDA; LLAMDAl is the log of LAMDAl; NDCDT is the change in concentration of a with respect to time and is used to determine reaction order with respect to time; LNDCDT is the log of NDCDT; CONA is the concentration of a; FML, FML1, FML2, FMT1, FMT2, and FML3 are format arrays for titles and table headings; ELCF is the cell volume of cell 1 or 2; LCONA is the log of CONA; CPIPXM is the concentration of the piperidinium halide in moles/l; CPIPX3 is a variable counter for CPIPX; LLAMD2 is the log of LAMD2.

C A is concentration, MW is molecular weight of DNXB; GRAMS is the amount of DNXB weighed out; CO is the initial conductance; CINF is the conductance at time infinity; KNCELL is the cell number 1 or 2; CELLK is the cell constant; N is the number of time data to be entered; L is the number of observations made at time less than 1 minute; TEMP is the temperature the reaction was run at.

## Main Program

```
      C  FRED MOOSREINER THESIS WORK CHEMISTRY DEPARTMENT
0001       DIMENSION CELL (2)
0002       DIMENSION X(25),Y(25),FMT(10),TITLE(8,10)
0003       DIMENSION M(25),TIME(25),CT(25,6),   MEAN(25), STNDEV(25),
           1STDVMN(25),DEVIM(6),DCTDT(6),DEVCT(6),DEVCT2(6),W(6),SCT(6),2
           1CONDRT(25),CXTOCA(25),CPIPX(25),RCPIPX(25),LCPIPX(25),
           1ALEFT(25),LALEFT(25),KAPPA(25),KAPPA1(25),LAMDA(25),CI95(25),
           1LAMDA1(25),LLAMDA(25),LLAMD1(25),NDCDT(25),LNDCDT(25),CONA(25),
           1FML(10),FML1(10),FML2(5),FMT1(10),FMT2(10),FML3(5),ELCF(2),
           1 LCONA(25),CPIPXM(25),CPIPX3(25),LLAMD2(25)
0004       EQUIVALENCE (M,X),(STNDEV,Y)
0005       EQUIVALENCE (DEVTM,DEVCT,DEVCT2),(CONA,LCONA),(NDCDT,LNDCDT)
0006       REAL LIST,MINUS
0007       REAL KAPPA,KAPPA1,LCPIPX,LALEFT,LAMDA,LAMDA1,LLAMDA,LLAMD1,
           1MW,LNDCDT,NDCDT,MEAN,MARI,LOW,LCONA,NUMCR
0008       DATA SENT / -1./
0009       DATA W(1),W(2),W(3),W(4),W(5),W(6) /-1.0,0.89,0.59,0.49,0.43,0.40/
0010       DATA TEST /:YX
0011       DATA PLUS,MINUS,LIST / 3H + ,3H - ,8HLIST /
0012       DATA XY,EOFS,NR,IT / :XY:,-1.,4,1 /
0013       DO 103 I1=1,7
0014       READ(2,201) (TITLE(I1,J3),J3=1,10)
0015   103 CONTINUE
0016       READ(2,996) CELL(1),CELL(2)
0017    11 READ(2,101) A,MW,GRAMS,CO,CINF,KNCELL,CELLK,N,L,TEMP
0018       READ(2,201)(FMT(I),I=1,10)
0019       WRITE(3,899)
0020       WRITE (3,202) FMT
0021       WRITE(3,203)
0022       DO 30 I = 1, N
        C  READ M THE NO. OF OBSERVATIONS AT EACH TIME
0023       READ (2,300) M(I)
0024            JM = M(I)
0025       READ (2,401) TIME(I), (CT(I,J), J=1,JM)
0026       WRITE (3,500) TIME(I), (CT(I,J), J=1,JM)
0027    30 WRITE(3,550) M(I)
0028       WRITE(3,204)
0029       READ(2,996) ELCF(1),ELCF(2)
        C  TIME AND CONDUCTANCE MEASUREMENTS FOR EACH CONCENTRATION PRINTED
        C  CALCULATE CT MEAN AND TIME MEAN FOR TIME LESS THAN 1 MINUTE
0030       DO 51 I = 1, N
0031            SUMCT = 0.0
0032            JM = M(I)
0033            SM = JM
0034       DO 41 J=1,JM
0035    41      SUMCT = SUMCT + CT(I,J)
0036    51      MEAN(I) = SUMCT / SM
0037       IF (L.EQ.1) GO TO 83
0038       CONTINUE
        C  CALCULATE STATISTICS FOR TIME LESS THAN 1 MINUTE
0039       DO 111 I = 2, L
```

```
0040            JM = M(I)
0041            SM = JM
0042            SUMDEV = 0.0
0043          DO 61 J = 1,JM
0044            DEVTM(J) = MEAN(I) - CT(I,J)
0045            DCTDT(J) = (TIME(I) - TIME(I-1))/(MEAN(I) - MEAN(I-1))
              C  DEVTM IS DEVIATION IN TIME, DCTDT IS CHANGE IN CONDUCTANCE PER
              C  CHANGE IN TIME
0046            DEVCT(J) = DCTDT(J) * DEVTM(J)
              C  DEVCT IS THE DEVIATION OF CT FORM A PRESET VALUE FOR TIME
              C  LESS THAN 1 MINUTE.  IT MEASURES ERROR IN SYRINGE INJECTION
              C  AND SMALL VOL VART.
0047            DEVCT2(J) = (DEVCT(J)) ** 2
0048     61     SUMDEV = SUMDEV + DEVCT2(J)
0049          STNDEV(I) = SQRT(SUMDEV/(SM-1))
0050            STDVMN(I) = STNDEV(I)/ SQRT(SM)
              C  STANDARD DEVIATION OF THE MEAN CALCULATED
              C  CALCULATE 95 PER CENT CONFIDENCE INTERVAL
0051          DO 65 J = 1, 6
0052     65     SCT(J) = -838607
0053            K = JM
0054          DO 71 J = 1,JM
0055     71     SCT(J) = DCTDT(J) *CT(I,J)
0056            HIGH =AMAX1(SCT(1),SCT(2),SCT(3),SCT(4),SCT(5),SCT(6))
0057          DO 75 J = 1, 6
0058     75     SCT(J) = +838607
0059          DO 80 J = 1,JM
0060     80     SCT(J) = DCTDT(J) * CT(I,J)
0061          LOW = AMIN1(SCT(1),SCT(2),SCT(3),SCT(4),SCT(5),SCT(6))
0062    111     CI95(I) = (HIGH-LOW) * W(K)
              C  CHANGE ARRAYS TIME AND MEAN FOR VALUES LESS THAN 1 MINUTE
0063     83   DO 110 I = 1, L
0064            MARI = MEAN(I)
0065            MEAN(I) = TIME(I)
0066    110     TIME(I) = MARI
              C  CONTINUE ON THE REST OF THE ARRAY TIME = TIME,CT = CONDUCTANCE
              C  AT TIME T
0067            L1 = L = 1
0068          DO 211 I = L1, N
0069            JM = M(I)
0070            SM = JM
0071            SUMDEV = 0.0
0072          DO 120 J = 1,JM
0073            DEVCT(J) = MEAN(I) - CT(I,J)
0074            DEVCT2(J) = (DEVCT(J)) ** 2
0075    120     SUMDEV = SUMDEV + DEVCT2(J)
0076            STNDEV(I) = SQRT (SUMDEV/(SM-1))
0077            STDVMN(I) = STNDEV(I)/ SQRT(SM)
0078          DO 125 J = 1, 6
0079    125     SCT(J) = -8388607
0080          DO 130 J = 1,JM
```

```
0081   130       SCT(J) = CT(I,J)
0082             HIGH =AMAX1(SCT(1),SCT(2),SCT(3),SCT(4),SCT(5),SCT(6))
0083         DO 135 J = 1, 6
0084   135       SCT(J) = +8388607
0085             K = JM
0086         DO 140 J = 1,JM
0087   140       SCT(J) = CT(I,J)
0088         LOW = AMIN1(SCT(1),SCT(2),SCT(3),SCT(4),SCT(5),SCT(6))
0089   211       CI95(I) = (HIGH - LOW) * W(K)
          C  STATISTICS ARE CALCULATED FOR ALL DATA POINTS
          C  NOW CALCULATE CONDUCTANCE RATIO AND RELATED FUNCTIONS
0090             IF (2 - KNCELL) 911,240,245
0091   240       J2 = 2
0092         GO TO 249
0093   245       J2 = 1
0094   249   CONTINUE
0095             NUMCR = CINF - MEAN(1)
0096         DO 250 I = 1, N
0097             CONDRT(I) =(NUMCR / (CINF - MEAN(I))) *1.0
0098             CXTOCA(I) = (MEAN(I) -CO) / NUMCR
0099             CPIPX(I) = CXTOCA (I) * A
0100             CPIPXM(I) = CPIPX(I) *ELCF(J2)
0101         RCPIPX(I) = SQRT(CPIPXM(I))
0102             ALEFT(I) = A - CPIPX(I)
0103             KAPPA(I) = CELLK * MEAN(I)
0104   250   CONTINUE
0105         READ(2,301) FML1
0106         READ(2,201) FMT1
0107         READ(2,205) FML2
0108         READ(2,201) FMT2
0109         READ(2,205) FML3
0110         WRITE(3,900)
0111         WRITE(3,910) FML1
0112         WRITE(3,920)
0113         WRITE(3,FMT1) A,FML2
0114         WRITE(3,FMT2) KNCELL,TEMP,FML3
0115         WRITE(3,960)
0116         WRITE(3,965)
0117         WRITE(3,903)
0118         WRITE(3,800) (TIME(I), MEAN(I), STDVMN(I),CI95(I),CONDRT(I),
             1I=2,N)
0119         WRITE(3,901)
0120         WRITE(3,970) CD,CINF
0121         WRITE(4,2000)      (TIME(I),CONDRT(I),I=1,N),SENT
0122         SUM1=0.0
0123         SUM2=0.0
0124         DO 260 I = 2, N
0125             LAMDA(I) =((1000*KAPPA(I))/(CPIPX(I)*ELCF(J2)))*0.0000010
0126         LAMDA1(I)=1000.*CELLK*((MEAN(I)/CPIPXM(I))-(((A-CPIPX(I))/A)*CO)/
             1(2*ALEFT(I)*ELCF(J2)))* 0.000001
0127         LCPIPX(I) = ALOG10(CPIPXM(I))
```

```
0128            CONA(I) =(ALEFT(I) + ALEFT(I-1))/2.0
0129            LCONA(I) = ALOG10(CONA(I))
0130          CPIPX3(I)=RCPIPX(I) *100.0
0131          LLAMD2(I)=1000./LAMDA1(I)
0132          LLAMDA(I) = CXTOCA(I) * 100.0
0133            LLAMD1(I) = ALOG10 (LAMDA1(I))
0134            NDCDT(I) = (ALEFT(I-1)-ALEFT(I))/(TIME(I)-TIME(I-1))
0135          SUM1=SUM1 +(STDVMN(I)/CT(I))*100.0
0136          SUM2= SUM2+ (CI95(I)/CT(I))*100.0
0137    260     LNDCDT(I) = ALOG10(NDCDT(I))
0138          SR=N
0139          SUMV1=SUM1/(SR-1.0)
0140          SUMV2=SUM2/(SR-1.0)
0141          CONTINUE
0142          WRITE(3,899)
0143          WRITE(3,994)
0144    994   FORMAT(31X,: TIME :,6X,:P/C RXN :,4X,:ROOT X:,5X,:KAPPA :,4X,
              1:LAMDA 1:,//)
0145          WRITE(3,990) (TIME(I),CXTOCA(I),RCPIPX(I),KAPPA (I),LAMDA1(I),I=1,
              1N)
0146          WRITE(3,967) SUMV1,SUMV2
0147          WRITE(4,2000) (LCONA(I), LNDCDT(I),I=2,N) ,SENT
0148          WRITE(4,2000) (TIME(I),MEAN(I),I=2,L),SENT
0149          WRITE(4,2000) (TIME(I),CPIPX(I),I=1,N),SENT
0150          WRITE(4,2000) (RCPIPX(I),LAMDA1(I),I=2,N),SENT
0151          WRITE(4,2000) (CPIPX3(I),LLAMD2(I),I=2,N)  ,SENT
0152          WRITE(4,2000) (TIME(I),LLAMDA(I),I=2,N),SENT
0153          CONTINUE
0154    101   FORMAT (1X,F9.8,2X,F6.2,2X,F6.4,2X,F6.2,2X,F8.2,2X,I1,2X,F6.4,
              12X,12,2X,I1,2X,F4.1)
0155    201   FORMAT(10A8)
0156    202   FORMAT(1X,///,25X,10A8)
0157    203   FORMAT(1H9,33X,:TIME:,10X,:CONDUCTANCE MEASUREMENTS:,34X,:M:,///)
0158    204   FORMAT(1H2,45X,:FOR TIME LESS THAN 1 MINUTE - TIME AND:,/,45X,:
              1CONDUCTANCE MEASUREMENTS ARE REVERSED,I.E.TIME VARIES:)
0159    205   FORMAT(5A8)
0160    300   FORMAT (2X,I1)
0161    301   FORMAT(10A1)
0162    401   FORMAT(2X,F6.2,6(2X,F10.2))
0163    500   FORMAT (31X,F8.2,6(3X,F9.2))
0164    550   FORMAT (1H+,105X,I1)
0165    800   FORMAT(31X,F7.2,2X,F10.2,2X,F7.2,3X,F7.2,7X,F8.3)
0166    899   FORMAT(1H1)
0167    900   FORMAT(1H1,90X,:XXX:,/,1H7,120X,:XXX:)
0168    901     FORMAT(1H2,30X,60(:-:),/,31X,60(:-:))
0169    903   FORMAT(31X,60(:-:),/)
0170    910   FORMAT(1H3,54X,:TABLE:,1X,10A1)
0171    920   FORMAT(1H4,30X,:AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS
              AT GIVEN TIMES:,1H:)
0172    960   FORMAT(1H3,30X,60(:-:),/,31X,60(:-:))
```

```
0173   965  FORMAT(43X,:AVERAGE C:,5X,:S:5X,:95 PER CENT:,5X,:C-C:,/,31X,:
            TIME IN:,9X,:IN:,7X,:---:,4X,:CONFIDENCE:,5X,:--------:,/,31X,
            :MINUTES:,5X,:MICROMHOS:,5X,:N:,6X,:INTERVAL:,7X,:C-C:)
0174   967  FORMAT(1H4,:AVERAGE PERCENT DEV. FOR STDVMN =:,410.5,4X,:AND
            FOR CI95 =:,F10.5)
0175   970  FORMAT(1H2,38X,:C:,2X,:=:,6X,F6.2,2X,:MICROMHOS:,7X,:THESE
            VALUES ARE:,/,74X,:CALCULATED FROM:,/,39X,:C:,2X,:=:,2X,F10.2,
            2X,:MICROMHOS:,9X,:ERRORS IN TIME:)
0176   990  FORMAT(31X,F8.2,F10.4,F10.5,2X,F10.2,F10.2)
0177   996  FORMAT(2X,F4.1,2X,F4.1)
0178  2000  FORMAT(2X,F13.6,2X,F13.6,2X,F13.6,2X,F13.6,2X,F13.6,2X,F13.6,
            2X,F13.6,2X,F13.6)
0179         REWIND 4
0180         I1=0
0181         IP = 0
0182         IF(IP.EQ.0) ID=1
0183      5  CONTINUE
0184         IF (IP.GT.0) ID=0
0185         J=1
0186         N=NR
0187         K=N
0188         IF(XY.EQ.TEST) GO TO 911
0189         IF (IT.EQ.1) GO TO 1515
0190  1515   READ(6,2000,END=704) (X(I),Y(I),I=J,K)
0191         DO 1517 I=J,K
0192         IF (X(I).EQ.EOFS) GO TO 704
0193  1517   CONTINUE
0194         J=J+N
0195         K=K+N
0196         GO TO 1515
0197   704   CONTINUE
0198         SUMX=0.0
0199         SUMY=0.0
0200         SXS=0.0
0201         SYS=0.0
0202         SMXY=0.0
0203         N=I-1
0204         DO 10 I=1,N
0205         WUMX=SUMX+X(I)
0206         SUMY=SUMY+Y(I)
0207         SXS=SXS+X(I)**2
0208         SYS=SYS+Y(I)**2
0209         SMXY=SMXY+(X(I)*Y(I))
0210    10   CONTINUE
0211         XMEAN=SUMX/N
0212         YMEAN=SUMY/N
0213         SMXSQ=SXS-(XMEAN*SUMX)
0214         SMYSQ=SYS-(YMEAN*SUMY)
0215         STDEX=SQRT(SMXSQ/(N-1))
0216         STDEY=SQRT(SMYSQ/(N-1))
0217         SUMXY=SMXY-(XMEAN*SUMY)
0218         RXY=SUMXY/SQRT(SMXSQ*SMYSQ)
0219         RXYSQ=RXY**2
0220         B=SUMXY/SMXSQ
```

```
0221          AZ-YMEAN-(B*XMEAN)
0222          AB = AZ
0223          IF (RXYSQ.LE. 1.0) GO TO 38
0224          RXYSQ=1.0
0225          STERR = SQRT((1.0-RXYSQ) / (N-2) * SMYSQ/SMXSQ)
0226          T=99999.9
0227          GO TO 39
0228       38 STERR = SQRT((1.0-RXYSQ) / (N-2) * SMYSQ/SMXSQ)
0029          T=B/STERR
0230       39 NDF=N-2
0231          I1=I1 + 1
0232          WRITE (3,40) (TITLE(I1,J3),J3=1,10)
0233       40 FORMAT(1H1,31X,10A8)
0234          WRITE(3,FMT1) A,FML2
0235          WRITE(3,FMT2) KNCELL,TEMP,FML3
0236          WRITE (3,50) N,XMEAN,¢MEAN,STDEX,STDEY,RXY,RXYSQ
0237       50 FORMAT(1H ,/////,10X,:N = :,I4,//,10X,:MEAN OF X = :,F15.3,
              //,10X,:MEAN OF Y = :
              ,F15.3,//,10X,:STANDARD DEVIATION OF X = :,F15.5,//,10X,:
              STANDARD DEVIATION OF Y = :,F15.5,//,10X,:R = :,F8.5,//,10X,:
              R SQUARED = :,F8.5)
0238          IF(AZ.LT.0.0) GO TO 60
0239          SGN=PLUS
0240          GO TO 70
0241       60 SGN=MINUS
0242       70 AB = ABS(AB)
0243          IF(ID.EQ.1) GO TO 73
0244          CONTINUE
0245          IF (ID.NE.1) GO TO 74
0246       73 RATE=((B)/(2*A))*(CELL(J2)/(1000.0))
0247          HALFL=1.0/B
0248          WRITE(3,100) B,SGN,AB,RATE,HALFL,STERR,T,NDF
0249      100 FORMAT(//,10X,:¢ = :,F12.6,: X :,A3,F12.4,10X,:RATE = :,F12.4,5X,
              :HALF LIFE =:,F8.2,//10X,:STANDARD ERROR OF REGRESSION COEFFICIENT
              = :,F12.8,//,10X,:T = :,F12.3,10X,:D.F. =:,I4)
0250          GO TO 434
0251       74 WRITE(3,116) B,SGN,AB,STERR,T,NDF
0252      116 FORMAT(//,10X,:¢ = :,F12.6,: X :,A3,F12.6,//,10X:STANDARD
              ERROR OF REGRESSION COEFFICIENT = :,F12.6,//,10X,:T = :,F8.3,
              10X,:D.F. = :,I4)
0253      434 WRITE (3,400)
0254      400 FORMAT (////10X,:OBSERVED:4X,:OBSERVED:,5X,:EXPECTED:,10X,
              :DIFFERENCE:,10X,:DIFFERENCE:,/,10X,:X-VALUE:,tX,:Y-VALUE :,
              5X,:Y-VALUE:,12X,:Y - MEAN:,10X,:Y - EXPECTED://)
0255          SSYD1 = 0.0
0256          SSYD2 = 0.0
0257          DO 600 I=1,N
0258          YY=B*X(I)+AZ
0259          YMMEAN = Y(I) - YMEAN
0260          YIMYY=Y(I)-YY
0261          SSYD1 = SSYD1 + YMMEAN * YMMEAN
```

```
0262          SSYD2 = SSYD2 + YIMYY * YIMYY
0263          IF(IP.EQ.3) GO TO 161
0264          GO TO 611
0265     161  WRITE(3,502) X(I),Y(I),YY,YMMEAN,YIMYY
0266     502  FORMAT(/,6X,F12.3,F12.6,1X,F12.6,6X,F12.6,6X,F12.6)
0267          GO TO 600
0268     611  WRITE(3,501) X(I),Y(I),YY,YMMEAN,YIMYY
0269     501  FORMAT(/,6X,F12.3,F12.3,1X,F12.3,6X,F12.3,6X,F12.3)
0270     600  CONTINUE
0271          WRITE(3,799) SSYD1,SSYD2
0272     799  FORMAT(:3:,14X,:SUM OF SQUARES OF DEVIATIONS:,3X,F15.3,3X,F15.3)
0273          WRITE(3,801)
0274     801  FORMAT(/1H1)
0275          CALL GRAPHS(N,X,Y,AZ,B)
0276          IP=IP+1
0277          IF(IP.EQ.7) GO TO 850
0278          GO TO 5
0279     850  IF(IT.EQ.1) REWIND 6
0280          GO TO 11
0281     911  END
```

```
0001        SUBROUTINE GRAPHS (N,Y,X,AZ,B)
            C
            C  THIS SUBROUTINE WILL PLOT A ONE PAGE GRAPH ON THE PRINTER.
            C
0002        DIMENSION K(26),X(1),Y(1),XWRD(11),YWRD(13),NN(4),KN(4),IZ(4)
0003        DATA LANK /4H    /,IDOT /4H    /,NN(1),NN(2),NN(3),NN(4)
              / 4H3000,4H0300,4H0030,4H0003 /,KN(1),KN(2),KN(3),KN(4)
              / 4H+   ,4H +  ,4H  + ,4H   + /,IDSH / 4H   - /,IZ(1),IZ(2),
             IZ(3),IZ(4) /4H1000,4H0100,4H0010,4H0001 /
0004        CALL SORT2 (X,Y,N)
0005        XRNGE=X(N)-X(1)
0006        YMAX=Y(1)
0007        YMIN=Y(1)
0008        DO 50 I=2,N
0009        IF(Y(I).LT.YMIN) YMIN=Y(I)
0010     50 IF(Y(I).GT.YMAX) YMAX=Y(I)
0011        YRNGE=YMAX-YMIN
0012        XWRD(1)=X(1)
0013        XWRD(11)=X(N)
0014        YWRD(1)=YMIN
0015        YWRD(11) = YMAX
0016        AY=0.1*YRNGE
0017        AX=0.1*XRNGE
0018        DO 60 I=2,10
0019        XI=I-1
0020        XWRD(I)=XWRD(1)+XI*AX
0021     60 YWRD(I)=YWRD(1)+XI*AY
0022        J=1
0023        J1=0
0024        JJ=1
0025        XL=0.2*AX
0026     90 XJ=J1
0027        DO 100 I=1,21
0028    100 K(I)=LANK
0029    110 IF(J.GT.N) GO TO 200
0030        IF ((XWRD(1) + (XJ + 0.001) * XL) .GT. X(J)) GO TO 200
0031        C=(Y(J)-YWRD(1))/AY
0032        JB=IFIX(C)
0033        NB=IFIX(C*2.)
0034        C=((Y(J)-YWRD(JB+1))/AY)*8.
0035        LOC=IFIX(C)+1
0036        IF(LOC.GT.4) LOC=LOC-4
0037        J=J+1
0038        IF(K(NB+1).NE.LANK) GO TO 190
0039        K(NB+1)=KN(LOC)
0040        GO TO 110
0041    190 K(NB+1)=K(NB+1)+NN(LOC)
0042        GO TO 110
0043    200 IF(J1.EQ.0) GO TO 250
0044    210 MJ=J1
0045    220 IF(MJ-5)270,240,230
0046    230 MJ=MJ-5
```

```
0047          GO TO 220
0048     240  JJ=JJ+1
0049     250  CONTINUE
0050          GO TO 400
0051     255  WRITE (3,260) XWRD(JJ),IDSH,(K(I),I=1,21)
0052     260  FORMAT (E18.6,A4,25A4,A1)
0053          GO TO 290
0054     270  WRITE (3,280) IDSH,(K(I),I=1,21)
0055     280  FORMAT (18X,A4,25A4,A1)
0056     290  J1=J1+1
0057          IF(J.GT.N) GO TO 300
0058          GO TO 90
0059     300  IF(JJ.GE.11) GO TO 500
0060          DO 310 I=1,21
0061     310  K(I)=LANK
0062          GO TO 210
0063     400  CONTINUE
0064          Z= (XWRD(JJ)-AZ)/B
0065          IF(Z.FT.YMAX) GO TO 255
0066          IF(Z.LT.YMIN) GO TO 255
0067          C=(Z   -YWRD(1))/QY +0.0000001
0068          JB=IFIX(C)
0069          NB=IFIX(C*2.)
0070          C=((Z   -YWRD(JB+1))/AY)*8. +0.0000001
0071          LOC=IFIX(C)+1
0072          IF(LOC.GT.4) LOC=LOC-4
0073          K(NB+1)=K(NB+1)+IZ(LOC)
0074          GO TO 255
0075     500  CONTINUE
0076          DO 70 I=2,22,2
0077          K(I)+IDOT
0078      70  K(I=1)=LANK
0079          WRITE (3,80)(K(I),I=1,22),(YWRD(I),I=1,11,2),(YWRD(I),I=2,10,2)
0080      80  FORMAT(15X,22A4,/12X,6(4X,E12.6)/20X,5(4X,E12.6)//57X,
              :X - A X I S:)
0081          RETURN
0082          END
```

```
0001          SUBROUTINE SORT2(A,B,N)
              C
              C  THIS SUBROUTINE SORTS A 1-DIMENSIONAL FLOATING
              C  POINT ARRAY (A), AND DUPLICATES THE RECORDING
              C  IN A SECOND ARRAY (B).
              C
0002          DIMENSION A(1),B(1)
0003          IF(N.LE.1) RETURN
0004          DO 20 I=2,N
0005          IM1=I-1
0006          DO 10 J=1,IM1
0007          JJ=I-J
0008          IF(A(JJ).GE.A(JJ+1)) GO TO 20
0009          X=A(JJ)
0010          A(JJ)=A(JJ+1)
0011          A(JJ+1)=X
0012          X=B(JJ)
0013          B(JJ)=B(JJ+1)
0014       10 B(JJ+1)=X
0015       20 CONTINUE
0016          RETURN
0017          END
```

# APPENDIX II

The analysis of variance for the data listed in Table XLVII was calculated using the following formulation. The grouping of the data does not lend itself to the simpler types of ANOVA cell arrangement and appreciation is acknowledged to Dr. Emery Sadler, formerly of the Psychology Department, for developing the formulation used.

C = concentration

D = cell

E = experimenter (or method)

The sum of the squares terms for each source of variation examined are:

C, df = c-1 = 2

$$SS_C = \frac{\sum(\sum\sum X_{ijk})^2}{de}^{C\ DE} - \frac{(\sum\sum\sum X_{ijk})^2}{cde}^{CDE}$$

$$= \frac{(1.646 + 1.524 +\ldots+ 1.738)^2 +\ldots+ (1.816 +}{(2)(3)}$$

$$\underline{1.661 +\ldots+ 1.594)^2} - \frac{(1.646 +\ldots+ 1.594)^2}{2(3)(3)}$$

D, df = d-1 = 2-1 = 1

$$SS_D = \frac{\sum(\sum\sum X_{ijk})^2}{ce}^{D\ CE} - \frac{(\sum\sum\sum X_{ijk})^2}{cde}^{CDE}$$

$$= \frac{(1.646 + \ldots + 1.627)^2 + (1.597 + \ldots + 1.594)^2}{1(3)(3)} - \text{(The}$$

same second term as above.)

E, df = 3-1 = 2

$$SS_E = \frac{\overset{E\ CD}{\sum(\sum\sum X_{ijk})^2}}{cd} - \frac{\overset{CDE}{(\sum\sum\sum X_{ijk})^2}}{cde}$$

CD, df = (c-1)(d-1) = cd-c-d+1 = 2

$$SS_{CD} = \frac{\overset{CD\ E}{\sum\sum(\sum X_{ijk})^2}}{e} - \frac{\overset{C\ DE}{\sum(\sum\sum X_{ijk})^2}}{de} - \frac{\overset{D\ CE}{\sum(\sum\sum X_{ijk})^2}}{ce} + \frac{\overset{CDE}{(\sum\sum\sum X_{ijk})^2}}{cde}$$

CE, df = (c-1)(e-1) = ce-c-e+1 = 4

$$SS_{CE} = \frac{\overset{CE\ D}{\sum\sum(\sum X_{ijk})^2}}{c} - \frac{\overset{C\ DE}{\sum(\sum\sum X_{ijk})^2}}{ce} - \frac{\overset{E\ CD}{\sum(\sum\sum X_{ijk})^2}}{cd} + \frac{\overset{CDE}{(\sum\sum\sum X_{ijk})^2}}{cde}$$

DE, df = (d-1)(e-1) = de-d-e+1 = 2

$$SS_{DE} = \frac{\overset{DE\ C}{\sum\sum(\sum X_{ijk})^2}}{c} - \frac{\overset{D\ CE}{\sum(\sum\sum X_{ijk})^2}}{ce} - \frac{\overset{E\ CD}{\sum(\sum\sum X_{ijk})^2}}{cd} - \frac{\overset{CDE}{(\sum\sum\sum X_{ijk})^2}}{cde}$$

CDE, df = (c-1)(d-1)(e-1) = cde-cd-ce-de+c+d+e-1 = 4

$$SS_{CDE} = \frac{\sum\sum\sum (X_{ijk})^2}{1}^{CDE} - \frac{\sum\sum (\sum X_{ijk})^2}{e}^{CD\ E} - \frac{\sum\sum (\sum X_{ijk})^2}{d}^{CE\ D} - \frac{\sum\sum (\sum X_{ijk})^2}{c}^{DE\ C}$$

$$+ \frac{\sum (\sum\sum X_{ijk})^2}{de}^{C\ DE} + \frac{\sum (\sum\sum X_{ijk})^2}{ce}^{D\ CE} + \frac{\sum (\sum\sum X_{ijk})^2}{dc}^{E\ DE} - \frac{(\sum\sum\sum X_{ijk})^2}{cde}^{CDE}$$

The F test values are calculated by dividing the MS term by the appropriate error MS.

$$F_C = \frac{MS_C}{MS_{CD}}, \quad F_E = \frac{MS_E}{MS_{DE}}, \quad F_D = \frac{MS_D}{MS_{CD} + MS_{DE} - MS_{CDE}}$$

$$F_{CD} = \frac{MS_{CD}}{MS_{CDE}}, \quad F_{CE} = \frac{MS_{CE}}{MS_{CDE}}, \quad F_{DE} = \frac{MS_{DE}}{MS_{CDE}}$$